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## THE RELATION OF OXIDATION TO THE ORIGIN OF SOFT IRON ORES OF MICHIGAN.


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ABSTRACT.

The processes which affected the development of soft iron ores in the Marquette and Gogebic ranges were examined and evaluated by petrographic and chemical techniques. By tracing oxidation through mineral transitions from original rock to ore the conclusion was reached that soft iron ores of

these two ranges were the result of mildly alkaline hydrothermal solutions acting upon silicated iron formations for a long period of time.

Oxidation, as exhibited by major and minor minerals of the iron formation, was the initial step in the development of soft ores. Alterations and oxidation of other rocks affected by the ore forming solutions confirm the processes recognized in the iron formation. Some of the reactions that took place during oxidation were evaluated according to the most recent thermodynamic data.

The steps in soft ore origin on these two ranges are commonly multiple and overlapping; however in their most simple form they are: 1) silication of the original iron formation, 2) oxidation of silicate formation, and 3) leaching of silica from the oxidized silicate rock. The last two steps were brought about by hydrothermal solutions.

## INTRODUCTION.

THE geologic processes that concentrated the soft iron ores of the Negaunee formation of the Marquette range, and the Ironwood formation of the Gogebic range, have been the source of investigation and speculation for more than a century. Of the many theories of ore formation presented throughout this period, only two are supported at present; they are the weathering theory formulated by Van Hise and Leith (70), and the hydrothermal theory presented by Gruner (28). Whereas the two theories disagree as to the method of ore formation, they do agree that solutions acting on the original siderite-cherts oxidized the iron and leached the silica to form soft ores. The recent observations by Tyler (66) that soft ores in the Marquette and Gogebic ranges were developed from metamorphosed iron formation rather than from the siderite-cherts, disturbs the sequence, and, in part, the chemistry of both the weathering and the hydrothermal theories.

In order to reevaluate the weathering and hydrothermal theories in light of Tyler's observation, a petrographic, mineralogical, and chemical study of the processes of oxidation and associated reactions effective in soft ore formation was conducted in the eastern Marquette and eastern Gogebic ranges by the present author. In the Marquette range, attention was focused on the soft ores of the Negaunee and Goose Lake formations; the soft ores of these formations are confined to the area east of an imaginary line with runs essentially southeast from the town of Clowry. Soft ores in the Marquette district west of this line, have been recognized only in the Bijiki formation. The Ironwood formation of the Gogebic range was studied only from the town of Wakefield east of the Vicar mine; however this section includes the area considered by Irving (37) to be typical for the range, for he said: "The chemistry of the process of concentration of the ore deposits east of Sunday Lake is, in all probability, like that of the typical deposits of the range."

The conclusions drawn from the present study of oxidation and related reactions are that the Negaunee and Ironwood iron formations of Michigan have been altered and oxidized to soft ores by solutions which were in part, if not predominantly, hydrothermal.

### VIEWS REGARDING SOFT ORE DEVELOPMENT IN THE MARQUETTE AND GOGEBIC RANGES.

*General Statement.*—The weathering and hydrothermal theories as now applied to the Marquette and Gogebic ranges are a result of the investigations, observations, and conclusions of many geologists. Therefore, a summary is presented of the various views regarding ore formation in these two ranges. Three papers—Van Hise and Leith (70), Gruner (28), and Tyler (66)—have been selected as milestones, because each summarized one phase of thought in regard to oxidation and each introduced another.

*Gogebic Range.*—Few reports published before 1892 discussed the origin of the ore of the Gogebic range. Most prospectors who found soft ores on

INDEX MAP OF UPPER MICHIGAN

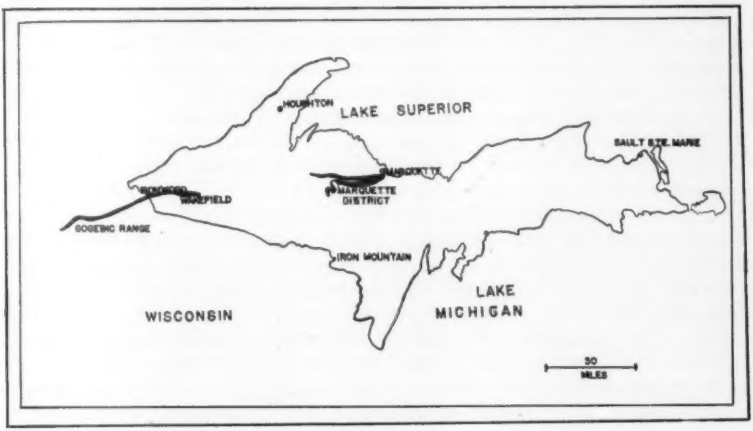


FIG. 1.

this range were guided by no single theory of ore development, and for the most part, geologists were concerned with the important problems of stratigraphy, lithology, and nomenclature.

The first hypothesis as to the genesis of ore on this range was ventured by T. C. Chamberlin (10), who suggested that the iron oxides were bog ores. Three years later C. E. Wright (79) concluded that the process of ore formation was one in which early minerals of the iron formation had been replaced by iron oxides. In the same year Irving (37) argued that during ore development some of the iron minerals had been oxidized in place while other iron oxides had been deposited from solutions. Irving's general theme was extended later to other ranges by Van Hise (68).

U. S. G. S. Monograph 19 by Irving and Van Hise (38) was the first

comprehensive report published on the geology of the Gogebic range. The conclusions presented in this paper were the result of five years of extensive field and petrographic studies of the range. Most of the rocks examined were near-surface specimens (38, p. 90, 293), because intensive mining developments on this range began in 1884, the year this survey was initiated.

The process of ore formation offered by Irving and Van Hise (38, p. 295) was an expansion of the theory presented by Van Hise in 1889. Whereas Irving and Van Hise (38, p. 285) considered that the ore-forming process was unique, they recognized that this was only one of the many ways in which the iron formations had been altered. As a consequence they (38, p. 190) divided the iron-bearing rocks into three types—in addition to soft ore—and discussed the origin of each; their classification was: 1. Cherty iron carbonate and siderite slates, 2. Actinolite slates, 3. Ferruginous slates and ferruginous cherts, and 4. Iron ore.

Irving and Van Hise (38, p. 246) concluded that the siderite slates are the original rocks of the iron formation, and thus are the antecedent of all other types. They (38, p. 257) considered that the other unoxidized type—actinolite slate—was derived from the siderite slates by an anamorphic process which involved both silication and the formation of magnetite. The other facies were regarded by Irving and Van Hise (38, p. 253, 256, 283) as the oxidized equivalents of siderite slates. They concluded that the ferruginous slates were derived from siderite slates by direct oxidation of the iron minerals; and that ferruginous cherts were formed from the same rock by partial oxidation of the siderite and replacement of the remainder of the minerals by silica.

Irving and Van Hise (38, p. 283) further believed that ore formation was a combination of oxidation, replacement, and deposition, for they state: "The iron carbonate has decomposed in place to iron oxide, the rock becoming a hematitic chert. Along the seams waters bearing iron in solution have passed. These waters have particle by particle dissolved out the chert and replaced it with iron oxides and where once was lean siderite rock is rich ore."

Moreover they say (38, p. 295): "Percolating water was the active agent of concentration. It has taken carbonate into solution and in its passage downward has been deflected into the troughs by the impervious quartz-slate formation and dikes. . . . In the apices of these troughs other waters more directly from the surface, bearing oxygen, have precipitated the iron as an oxide."

*Marquette Range.*—Although many varieties of iron ores were noted by Foster and Whitney (17) and other early students of the Marquette district, it was not until Brooks' (8) study of the range was published that geologists considered in a serious manner the origin of soft ores as distinct from the origin of hard ores of the district.

Foster and Whitney (17, p. 67–69) expressed the opinion, which was later reaffirmed by Whitney (77) that the ores of the Marquette district were of igneous derivation. The conclusion by Kimball (41) that the ores were formed by sedimentary processes, was greatly influenced by his views regarding hard ores. In 1873, Brooks (8, p. 220) classified the ores into five varieties; one of these was a soft ore which he believed was formed by removal of silica by thermal waters. The following year, Newberry (57) suggested that

the ores of the Marquette district were derived from sediments by the processes of erosion.

In a series of papers M. E. Wadsworth (71, p. 51; 74, p. 142–143) presented the theory that the soft ores of the district resulted from the action of hot waters on ferruginous schists. Such views were directly opposed to the opinions of Rominger (61, p. 75) as well as to those of Irving and Van Hise (38, p. 125), for these men maintained that the soft ores of the range were formed by processes of erosion acting upon siderite-cherts much in the same manner as they described for the Gogebic range.

Monograph 28, published in 1897, represented nearly five years' field and petrographic study of the Marquette range by Van Hise, Bayley, and others. The theories offered in Monograph 28 (69, p. 403) for oxidation and leaching of the iron formation to soft ores were essentially the same as those presented in Monograph 19. Van Hise and Bayley found rock types associated with soft ores in the Marquette range to be primarily the same as those of the Gogebic range, for they (69, p. 337) stated: "It is unusual to find exposures of the cherty siderite-slates which have not been more or less affected by deep-seated alteration or by weathering processes. As a consequence the iron carbonates pass by gradation on the one hand into grunerite-magnetite-schists, and on the other into ferruginous slates, ferruginous chert, jasper, or iron ore."

Thus they recognized and described (69, p. 336) jasper, or jaspilite, as another rock type of the iron formation. "The jaspilite differs mainly from the ferruginous chert with which it is closely associated, in that the siliceous bands of the former are stained a bright red by hematite, and the bands of ore between them are mainly specular hematite, while in the cherts the iron oxide is earthy hematite."

In regard to the development of ore, Van Hise and Bayley (69, p. 403) said: "Surface waters bearing oxygen, passing downward through the Upper Marquette series or the iron-bearing formation of the Lower Marquette series, would decompose the iron carbonates with which they came in contact and thus become carbonated. . . . The downward moving waters passed along and through the beds of iron-bearing formation until they came in contact with an impervious substance. Here were also converged oxygen-bearing waters more directly from the surface. The union of these two currents precipitated the iron oxide."

*Marquette and Gogebic Ranges.*—In their comprehensive treatise on the Lake Superior region, Van Hise and Leith revised and summarized the geology of the Marquette and Gogebic ranges. The theory which they presented (70, p. 242) for soft ore development in the Marquette and Gogebic ranges followed closely the steps outlined by Irving and Van Hise. Moreover, Van Hise and Leith recognized that the soft ores of the Negaunee and Ironwood formations were produced by the same processes; for they (70, p. 276) said: "The soft ores and associated ferruginous cherts of the middle and lower horizons of the Negaunee formation are similar physically, chemically, and mineralogically to the ores of the Penokee-Gogebic district. They are derived by the same processes, under the same conditions, from cherty iron carbonate rocks which are practically identical with those of that district."

INDEX MAP OF THE MARQUETTE DISTRICT

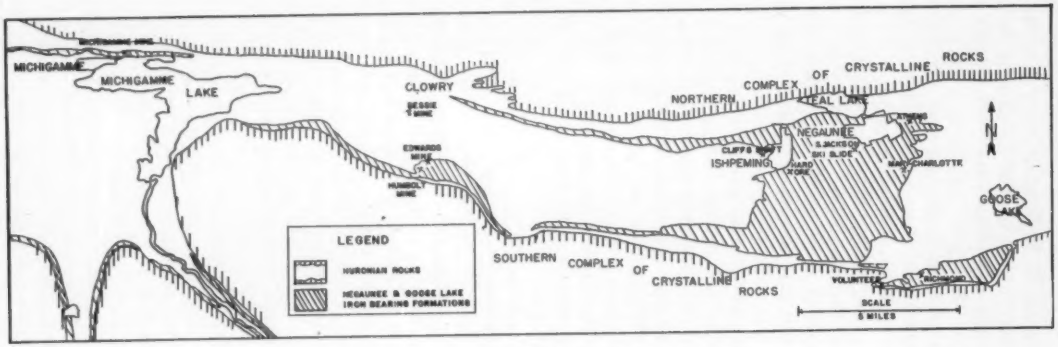


FIG. 2.

Van Hise and Leith (70, p. 231, 263) classified the iron-bearing rocks into four types, exclusive of ore: 1) siderite-cherts and slates, 2) ferruginous cherts and slates, 3) jaspilite, and 4) silicate-magnetite rocks. The classification and interpretation of each variety differed from earlier descriptions only in regard to ferruginous cherts. About these they (70, p. 263) said: "From the oxidation of the less slaty phases of the siderite rocks result the ferruginous chert, consisting mainly of alternating layers of chert and iron oxide. . . ."

The steps in the process of ore formation presented by Van Hise and Leith (70, p. 243) are the same as those outlined by Irving and Van Hise (38, p. 295); however, more emphasis was placed by Van Hise and Leith on oxidation *in situ* of iron minerals, and less emphasis was placed on transportation of iron. They (70, p. 243) outlined a sequence of ore development as follows: "The alteration of the cherty iron carbonates to ore has been accomplished in the general manner already described as typical for the region—1. oxidation and hydration of the iron minerals in place, 2. leaching of silica, and 3. introduction of secondary iron oxide and iron carbonate from other parts of the formation." Furthermore they considered that the alterations were effected by supergene solutions, for they (70, p. 528) said: "The essential secondary changes in the devolpment of the ores have been effected by weathering," and (70, p. 540): "In general the same processes of weathering that have produced the residual clays from igneous rocks are the ones which have secondarily concentrated the iron ores."

During the period of 1911 to 1937 Gruner proposed and developed a hydrothermal hypothesis for the origin of soft ores. Although many papers published during this period—such as those by Allen and Barrett (2), Hotchkiss (36), and Aldrich (1)—added much to the understanding of the iron formation, Gruner (24) introduced the first serious challenge to the Van Hise and Leith weathering theory of soft ore development when he (25, p. 697) suggested that: ". . . the hematite ores of the Soudan formation of the Vermilion range had been leached of silica and oxidized by hot ascending waters from a large basic magma."

In 1930, Gruner, interpreting the results of experiments on the solubility of silica and on oxidation of iron minerals, extended his hydrothermal hypothesis to soft ores; he (25, p. 864) said: "The experimental facts lend strong support to the hypothesis that the Lake Superior hematite-limonite ores were oxidized and leached hydrothermally." As field evidence for this hypothesis, Gruner (25, p. 837–867; 26) cited many examples in the Lake Superior iron ranges which were not explained satisfactorily by the weathering theory, but which could be identified readily with hydrothermal activity.

Leith (45, 46) compared critically the weathering theory and Gruner's hydrothermal hypothesis, and concluded that, with minor modifications, the weathering theory as expressed by Van Hise and Leith was adequate to explain soft ore formation in the major iron-bearing ranges of the Lake Superior districts.

Gruner (28), after listing 23 geological facts which must be explained by any theory of the origin of soft ore, concluded that 19 of these were opposed to the weathering theory, and the other four were opposed to a modified hy-

drothermal theory for soft ore development, which incorporated both supergene and hypogene fluids. Gruner's new theory did not alter his original opinion that the agent of oxidation and leaching was hot water, and that its direction of movement was toward the surface. He stated (28, p. 130): "It is proposed that the chief source of the hot waters was meteoric. The waters mingled with gaseous emanations that rose from large intrusives. . . . The emanations probably were largely superheated steam and as such were able to heat large quantities of meteoric water by the heat of condensation alone." To which he added: "The new theory is applicable to all iron ores of the Lake Superior type."

More recently Tyler (66) recognized a direct correlation between metamorphosed iron formation and soft ore development. His observations were greatly aided by Gruner's investigations of magnetite (22, 23), greenalite (27), stilpnomelane (29, 30), and minnesotaite (31). The identification of these minerals so extended the limits of petrography to the iron formations that Tyler (66, p. 1123) concluded: ". . . the ores were derived from a metamorphic facies, rather than directly from the original cherty iron formation. . . ."

This conclusion, although not a theory of ore formation, was shown by Tyler (66, p. 1104) to be a critical step in removal of silica during ore development; as such it must be included in the theory of the origin of soft ores.

*Summary of Views Regarding Ore Development.*—Today, the geologist prospecting for soft iron ores in the Marquette and Gogebic ranges, must follow either the weathering theory supported by Leith, or the hydrothermal theory presented by Gruner. Whereas these two theories agree that the siderite-chert rock was altered to form soft ores by oxidation of iron, leaching of silica, and addition of some iron, they disagree as to the method by which this was accomplished. Leith maintains that downward-moving surface waters, bearing oxygen in solution, were the effective agents, and Gruner contends that upward-moving, mixed meteoric and hydrothermal solutions accomplished the result. Tyler's observations that the metamorphosed facies of the iron formation was oxidized and leached to form ore, disrupts the initial tenet of both theories, although it does not directly effect the general structure of either method. Because this metamorphic principle was recognized by the present author to be a significant step in the ore-forming process, a reevaluation of both theories was undertaken in the Marquette and Gogebic ranges.

## MAJOR MINERALS OF THE IRON FORMATION AND THEIR ALTERATIONS.

*Introduction.*—Any conclusions as to whether the hydrothermal or weathering theory most clearly explains the origin of soft ore in the Negaunee and Ironwood formations depends upon the knowledge of at least two general geological facts: 1) the nature of the iron formations at the time of ore development, and 2) the nature of the effective solutions. Other factors such as intrusive, structural, and stratigraphic controls are clearly important in the genesis of the ore, but because every theory of ore formation points to such controls for supporting evidence, they cannot be understood so clearly at present, that they define uniquely any ore-forming process. Neither has the

specific study of the solubility of silica established a singular leaching solution. Investigations by Gruner (25), Lovering (51), Morey and Ingerson (56), Hitchen (35), Kennedy (39, 40), and many others have shown that silica solubility is a function of the silica mineral, its orientation, its purity, and its size, as well as the temperature, pressure, concentration, pH, and nature of the solution. Thus, regarding the *sine qua non* of ore formation, a wide range of geological solutions are capable of dissolving silica to some extent from the iron formation minerals. Furthermore, Tyler (66) has implied in his theory of metamorphism that silica removal is a function more of the condition of the iron formation at the time of ore development than of the nature of the solution. If this is true then the fact that all ore is oxidized, but not all oxidized formation is ore, does not preclude that the rocks were derived from the action of different solutions.

Thus, the nature of the ore process must be expressed by the reactions associated with oxidation, and revealed by the minerals themselves; these minerals—their existence, their associations, their transitions, and their degree of oxidation—must be a result of chemical and physical readjustment to thermodynamic systems. By tracing mineralogical and chemical transitions associated with oxidation from the original formation to ore by means of petrography and some chemical analyses, the present author concluded that on these two ranges, hydrothermal solutions were necessary, if not sufficient for the formation of soft ores.

The siderite-chert facies is recognized by the present author to be the predecessor of all other iron formation types; this is in agreement with Irving and Van Hise (38, p. 246), Van Hise and Bayley (69, p. 335), and Van Hise and Leith (70, p. 231). The generalized name—siderite-chert—includes sideritic cherts, cherty iron carbonates, and also siderite slates, for as Hotchkiss (36, p. 7) explained: ". . . , in many cases what is termed 'slate' in the iron formation in so called largely because of its thin, even bedding, . . . In most cases the true slaty material is a relatively insignificant part." The specific definitions applied to these names by Aldrich (1, p. 91) are avoided.

Siderite-cherts are generally fine-grained, highly laminated rocks that consist predominantly of chert and siderite. When unaltered they are commonly gray-white to pale blue-green, but when exposed to weathering they rapidly develop a thin coating of reddish-brown iron oxides. Although they possess an average specific gravity on the order of 3.5, and an average iron content of around 20–25 percent, individual specimens of siderite-cherts vary widely around these figures; considerable variations in both features of these rocks may be observed at the Athens mine outcrop near Negaunee. Excellent examples of uniform but finely laminated siderite and chert were acquired from recent drilling near the Mary Charlotte mine, whereas irregular fine banding was exhibited by core obtained from drilling near the Holmes mine. On the Gogebic range, all varieties of lamellar siderite-cherts may be observed in the vicinity of the Vicar mine; the bands vary from coarse and irregular to fine and even. One extreme facies of the iron formation may be seen in test pits north of the Bessie mine. Here, in the Bijiki formation, chert bands are so abundant that early workers mapped the formation as a quartzite.

*Minerals of the Siderite-Chert Rock.*—Siderite is the major ferrous iron mineral in the original iron formation of the Marquette and Gogebic ranges. Clear euhedral siderite rhombs varying in size from less than a micron to at least 3 mm across the short diameter are observed frequently; however the crystals more commonly are on the order of .05 mm. Because of the fine grain size no attempt was made to separate siderite from ferrodolomite. Distribution of the iron carbonates varies from nearly monomineralic bands of siderite, through siderite disseminated in chert bands, to nearly pure chert bands, with all gradations existing between the two extremes.

The term chert is used by the present author to denote extremely fine grained silica having the index of quartz, with no reference as to its origin (32, p. 17). In the siderite-cherts, chert is very fine grained—normally on the order of 5–10 microns—and commonly may be recognized only by aggregate index or birefringence. Distribution of chert in these rocks is essentially inversely proportional to that of siderite; however it seldom is absent in any band. Most commonly chert is a matrix to other minerals.

Greenalite was not identified in any specimens examined from the Marquette or Gogebic ranges. Leith (70, p. 231) states that minor amounts of this mineral were noted in the Ironwood formation of the Gogebic range, and Tolonen (64, p. 58) referred to greenalite at the Volunteer-Maitland mine at Palmer. As these are the only two to recognize greenalite on these ranges, the present author concluded that greenalite must be a minor mineral in the Marquette and Gogebic ranges.

Individual rhombs of dolomite commonly are found associated with siderite in the siderite-chert rocks; this statement applies also to the calcite-siderite relationship, as the distinction seldom could be made in thin-section between calcite and dolomite. Size, shape, and appearance of dolomite crystals was so similar to that of siderite that the carbonate aggregate was classified collectively as siderite. In such carbonate aggregates the quantity of dolomite that could be assigned a primary origin is small—on the order of 2 percent or less. More commonly dolomite is recognized as a secondary vein mineral.

Pyrite, commonly recognized in the siderite-cherts, may be original in part, but more generally is directly related to or in veins. Very fine-grained pyrite distributed in the carbonaceous and argillaceous facies of the siderite-cherts is most likely primary.

Carbonaceous material in the siderite-cherts, too fine grained for positive identification, was identified tentatively as graphite. In bands high in carbonates, black flakes were observed lining styolite-like structures. Black graphitic seams were noted in the more slaty facies of the siderite-cherts.

Apatite was the only phosphorus-bearing mineral identified in the siderite-cherts. Whereas the apatite in the Negaunee and Ironwood formations generally is subhedral and is very fine grained, the apatite in the Bijiki formation is as large as a millimeter or more; it is usually euhedral. Chemical spot tests on the original Negaunee and Ironwood formations after Mann (52) show that the phosphate distribution is stratigraphic, and that it is concentrated in variable proportions in the original beds; as such phosphorus is a minor original element in the iron formation, represented at least by apatite.

Whereas hematite and magnetite were noted in the original siderite-chert, the quantity of each oxide is small; there is little evidence as to the origin of these oxides. Frequently zoned siderite rhombs are encountered where one or more inner zones are predominantly hematite. Although this relation was noted in siderite-cherts that are slightly oxidized, it was not observed in completely unoxidized facies. No conclusions could be drawn as to whether this phenomenon occurred during deposition or during a later oxidation and carbonation process. Magnetite, associated with siderite, is present in at least minute amounts in nearly all slides of the siderite-cherts. More often than not, siderite showed evidence of alteration when associated with magnetite; where such alteration is not recognized, the magnetite may be primary.

Aphrosiderite was identified petrographically as a minor mineral in the siderite-cherts of the Negaunee and Ironwood formations, and probably should be listed as a primary mineral. As Winchell (78, p. 381) described aphrosiderite as one member of an isomorphous series of chlorites it is not surprising that Crump (13) recognized other members of the series—daphnite and thuringite. Although grains and elliptical blades, rarely larger than 5 microns, occur individually, aphrosiderite was found most commonly in aggregates. This chlorite replaces other iron silicates as well as siderite and chert; in turn it was found partly replaced by later silicates. Thus, aphrosiderite probably developed during diagenesis or during later metamorphism.

Of the minerals found in the siderite cherts of the Negaunee and Ironwood formations, the present author could recognize as definitely primary only siderite, chert, dolomite, and apatite. These are the minerals that were altered to form other facies of the iron formation. Other constituents, minor in amount, may be original in part, but more commonly may be shown to be secondary. As a consequence, hematite, goethite, magnetite, pyrite, aphrosiderite, and graphite are considered to be primary locally, but certainly secondary in most cases.

*Alteration of the Siderite-Cherts.*—The siderite-chert facies commonly is altered to silicate-magnetite rocks, as well as to one variety of ferruginous chert. The unoxidized silicate-magnetite rocks consist of various mixtures of magnetite and iron silcates with residual siderite and chert. When siderite has been replaced by hematite, or oxidized to goethite, the resulting rock is a ferruginous chert.

Several varieties of the silicate-magnetite facies occur on the eastern Marquette and eastern Gogebic ranges. Magnetite may be abundant or may be absent, whereas the silicates, minnesotaite, stilpnomelane, grunerite, or aphrosiderite may be abundant either individually or collectively. The alteration of siderite and chert to form iron silicates and magnetite represents a rearrangement of the iron and the silica of the original minerals. During silication, little if any iron was oxidized, whether it was present originally or was added during the process. Whereas silication could not always be separated in the field from later oxidizing processes, the abundance of unoxidized silicate-magnetite rocks cited by Tyler (66, p. 1112) in the areas under consideration testifies to the individuality of each process. The processes effective

in producing the silicate-magnetites are recognized more clearly when individual mineral transitions are considered.

The alteration of siderite to magnetite was recognized first from field and petrographic studies of rocks of the Gogebic range by Irving and Van Hise (38, p. 259), and on the Marquette range by Van Hise and Bayley (69, p. 419). Later Van Hise and Leith (70, p. 550) presented a discussion of the chemistry of this alteration.

Important quantities of magnetite have developed from siderite in the Negaunee and Ironwood formations. The pattern of the transition is well defined at the New Volunteer mine where basic dikes have cut the iron formation. In the original formation some distance from the dike, the magnetite content increases at the expense of the siderite. Previously unaltered cherty bands in which siderite is disseminated become more magnetic as the dike is approached. Tyler noted (66, p. 1106) that at this locality the silicate distribution followed closely the distribution of the magnetite.

The siderite-magnetite relations observed at the New Volunteer mine may be seen in the mildly altered siderite-cherts throughout the iron formations of both ranges. The transition of siderite to magnetite is best observed when magnetite is a minor constituent.

Magnetite occurs almost exclusively in and around siderite. When associated with magnetite, siderite rhombs rarely are fresh, clean, or euhedral; more often they are broken into fragments, each of which includes spots of magnetite. Tiny octahedra of magnetite are scattered between, in, and around the fragments. The general outline of the original rhomb may be recognized when only a portion of the siderite remains, for rims or shells of carbonates are common, each partly filled with magnetite. Whether a single crystal or an aggregate, magnetite is generally less than half the size of the original siderite crystal. When siderite is disseminated, so also is the magnetite.

When siderite is abundant in well defined bands, magnetite occurs in at least two manners; either it is disseminated in and around fragmental siderite rhombs, or it forms an undulatory band confined to the siderite bed. The line of magnetite crystals may be concentrated along the contact of a siderite-chert band, or it may be observed to thread the siderite band and cut siderite crystals. Commonly this siderite consists of a group of crystals appearing as a large subhedral crystal, with magnetite threading along the contacts of the individual fragments.

From thin-sections, it is evident that great quantities of magnetite have formed at the expense of siderite. Siderite appears to have fractured explosively with the escape of volatile constituents, leaving magnetite as a residue. Where siderite is abundant a stabilizing effect is noted; only a part of the siderite has changed to magnetite and the unaltered iron carbonate has been rearranged. There is no way at present of determining how much of this rearranged carbonate has been added from another part of the formation; however, in the same slides where siderite is disseminated in chert, magnetite is disseminated in and around the siderite. Such an arrangement indicates that much magnetite has been derived from siderite in the immediate vicinity.

The change in volume, almost 50 percent, resulting from the alteration

of siderite directly to magnetite was noted only in part. Both siderite and chert were rearranged so as to minimize the apparent voids, as shells of siderite rhombs were filled with chert or magnetite. Magnetite, arising in this manner, is common to rocks not otherwise oxidized; the oxide has developed with or without unoxidized silicates. Thus, magnetite appears to have developed from siderite within the rock autometamorphically—merely with the addition of heat.

In the Negaunee and Ironwood formations, under slightly different conditions from those above, a considerable amount of siderite has been altered to form iron silicates. All stages of the transitions may be observed from siderite-cherts that have only a few silicates, to rocks that are predominantly silicates. Of the various silicates that have been recognized in the iron formation, only four are considered by the present author to have been a factor in the soft ore development; they are stilpnomelane, minnesotaite, grunerite, and aphrosiderite.

In the Negaunee formation of the eastern Marquette range and the Ironwood formation of the eastern Gogebic range, minnesotaite and stilpnomelane are locally abundant and commonly the predominant iron silicate; aphrosiderite is a frequent associate. Grunerite is the most common iron silicate in the western Marquette range in both the Bijiki and Negaunee formations. Silicate distribution as well as some of the conditions favoring the development of one iron silicate over another have been discussed by Tyler (66). Because these reactions involve the iron minerals of the siderite-cherts, they are of importance to the study of oxidation.

The development of stilpnomelane and minnesotaite from siderite and chert is recognized most readily in bands where siderite is disseminated in chert; here minnesotaite and stilpnomelane occur in clusters confined to the immediate area around siderite. Whereas small fibrous silicates commonly enter and terminate within the siderite grains, large acicular crystals of minnesotaite and stilpnomelane may extend completely through the siderite rhombs. Siderite cleavage exerted no recognizable control on the silicate growth, for the fibers enter and leave siderite rhombs at all angles, without change in direction or in size. With the development of bundles and rosettes of stilpnomelane and minnesotaite, there is a marked decrease in the quantity of siderite. Silicate fibers, radiating from a common center, cut through one or more siderite crystals and divide them into irregularly sized fragments of all shapes. Generally where stilpnomelane and minnesotaite are significant rock constituents, the original siderite outlines may be recognized only by their aggregate polarization; however, in rocks that are mostly silicates, residual siderite, if recognized at all, is represented by a residual fragment interstitial to an interlocking mat of silicate fibers.

Grunerite is developed most extensively in the Negaunee and Bijiki formations of the western Marquette range. The occurrence of minerals such as garnets, chloritoid, and tourmaline in the Negaunee formation west of Humbolt, testifies that this area has been readjusted chemically to metamorphism which obliterates the early stages of grunerite development. Whereas the Bijiki formation also has undergone metamorphism, the genesis of grunerite

in the formation is not obscured. Excellent examples of the alteration of siderite and chert to grunerite were obtained from the soft ore pits of the Imperial, Beaufort, Portland, and Bessie mines. The silicates were developed in the Bijiki formation at the expense of siderite and chert, much in the same manner as minnesotaite grew in the Negaunee formation. Siderite rhombs were penetrated and separated into fragments by grunerite fibers, bundles, and rosettes, until siderite was used up. The ultimate of this silication is a rock composed entirely of grunerite, such as those specimens found on the dumps at the Imperial mine.

Aphrosiderite was recognized in all stages of replacement of siderite, from partly altered siderite rhombs to rhombs filled entirely with tiny flakes (.005 mm) of aphrosiderite. Commonly the replacement is directly associated with aphrosiderite-filled veinlets; in these cases aphrosiderite is highly developed near the vein and decreases in amount away from it. In places where aphrosiderite could not be related to a vein, it could have originated from diagenetic processes.

The role of chert in the development of secondary silicates has been emphasized by Tyler (66, p. 1104). As in the case of siderite, chert decreases in amount with an increase in silicates. Chert grains in contact with minnesotaite, stilpnomelane, or grunerite have irregular or jagged boundaries; commonly these grains are penetrated by the silicates. When these silicates are dominant constituents of the rocks, distinct grains of chert are rarely recognized.

Aphrosiderite commonly occurs as worm-like inclusions in chert grains, as well as along grain boundaries. The green color of many cherts obtained from the Tracy area in the Marquette range, and from the Vicar mine in the Gogebic range were caused by aphrosiderite occurring in this manner. The irregular boundaries of chert noted in the presence of other iron silicates—stilpnomelane-chert—could not be recognized in the aphrosiderite-chert relation; thus, the origin of aphrosiderite in the cherts of this type could be dated no closer than pre-oxidation. One example found in a drill core from the Mary Charlotte mine shows a siderite-chert rock containing aphrosiderite cut by later veins of stilpnomelane. Near the veins, stilpnomelane completely replaces aphrosiderite. All varieties of this veining and replacement of aphrosiderite by stilpnomelane were observed in rocks of the district.

The conditions that favored the development of stilpnomelane, minnesotaite, grunerite, and aphrosiderite from siderite and chert were essentially non-oxidizing to ferrous iron compounds. The reactions merely involved a physical and chemical rearrangement of the ferrous iron; thus they represent a readjustment to the superimposed conditions. The same kind of conditions favored the earlier, as well as simultaneous, development of magnetite directly from siderite. Although stilpnomelane, minnesotaite, and grunerite commonly are entwined around euhedral magnetite aggregates, no reaction between the silicates and magnetite has been recognized; that is, magnetite was not observed to have developed from these silicates, nor did these silicates develop from magnetite. Moreover, there was no evidence of a reaction between the silicates and magnetite to form yet another mineral; they were chemically inert to one

another under the metamorphic and later oxidizing conditions that affected them.

The direct alteration of iron carbonates of the siderite-cherts to hematite or goethite yields a variety of ferruginous cherts. Irving and Van Hise (38, p. 201) first recorded the metasomatic pattern of ferric oxides after siderite when they discussed the changes in the siderite-cherts near the Sunday Lake outlet on the Gogebic range. They stated: "Very frequently the decomposition of the iron carbonate has not changed the forms of the original crystals, and thus leave the various oxides as perfect pseudomorphs after the iron carbonate."

The specimens collected by Irving and Van Hise from which the above conclusions were drawn were reexamined in the course of this investigation. Thin-sections of these specimens, as well as samples from the siderite-cherts of the Castile mine near Wakefield, display the complete transition from clear siderite rhombs to rhombs filled with hematite and goethite. This type of alteration nearly always is related to fractures; if a traverse is made normal to and away from a joint surface, the rhombs filled with ferric oxides become fresh rhombs of siderite. All gradations exist between the two extremes. (Monograph 19, Pl. XXI, fig. 4.) The same type of alteration may be observed at Hard Ore No. 7 mine on the Marquette range; here hematite, controlled by a late fracture system, selectively replaced siderite bands, leaving chert bands untouched. In these transitions there is no evidence of a 50 percent volume decrease that would have occurred if the reaction was stochiometric.

In contrast, siderite-cherts exposed to the present erosion surface rapidly develop a thin skin of iron oxides. These oxides, in the early stages of oxidation, are pseudomorphous after siderite; however, on the highly oxidized surface there exists only a fine ferric oxide powder with little or no evidence of the former siderite rhomb. Examples of this type of alteration affecting partly silicated siderite-cherts at the Athens mine, the Ishpeming Ski Slide, and in test pits south of Negaunee, also show that silicates and magnetite are unoxidized under these surface conditions although they may be stained. This pattern of alteration that can be attributed directly to the present surface is unlike the pattern seen in deep drill cores, where oxidized silicates are commonly found in contact with unoxidized siderite.

Thus, the present author concluded that for the most part, ferric oxides have replaced siderite pseudomorphically without affecting other iron minerals or chert. Hematite, a mineral in a high state of oxidation, does result from an oxidation process; however the replacement of siderite by hematite does not appear to have been a direct result of oxidation, but rather of an oxidized solution. Such a metasomatic process might have been effective in producing the dense specular hematite deposits in the upper horizons of many soft ores in the Negaunee formation.

*Oxidation of Iron Silicate Magnetite Rocks.*—The processes effective in producing soft ores were superimposed upon most rock types of both the Negaunee and Ironwood formations. Whereas soft ore-forming processes were distributed locally along the Ironwood formation in Michigan, they were confined in the Negaunee formation to the area, east of a line running southeast from Clowry. Oxidation commonly was late in geologic history, follow-

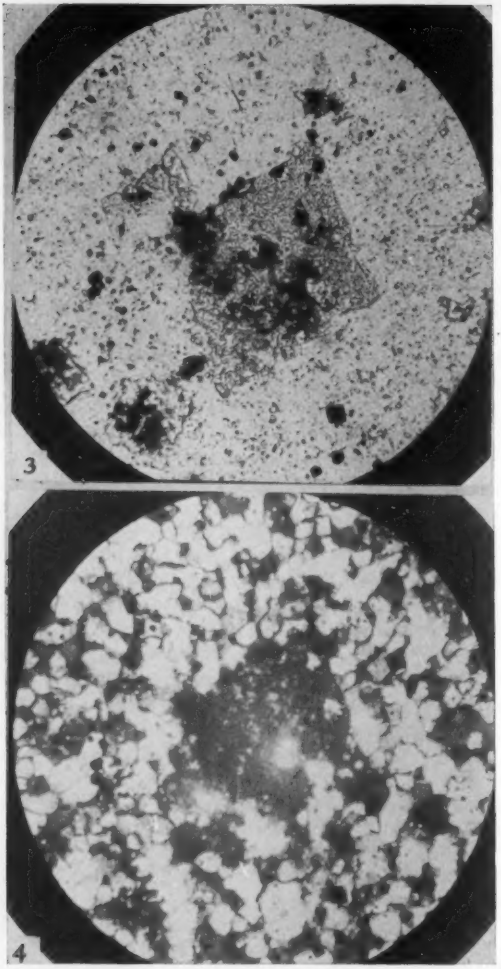


FIG. 3. Silicates oxidized in presence of unoxidized siderite. Siderite (white) replaced by aphrosiderite (gray) which is altered to hematite (black). Chert Matrix. WO analyzer, × 430, Sec. 7, T 46N, R 26W, Michigan.
FIG. 4. Same as 3, with analyzer.

ing silication in most cases, and affecting some hard ores in the Marquette district. The nature of the ore-forming process may be observed most readily in rocks intermediate between oxidized and unoxidized areas; these rocks—ferruginous cherts—mostly are oxidized silicate-magnetite facies.

Minnesotaite, stilpnomelane, grunerite, and aphrosiderite may be recognized in all stages of oxidation to either hematite or to hydrated hematites. Most commonly minnesotaite and grunerite altered to hematite; however, in places they were oxidized to goethite; the other two iron silicates—stilpnomelane and aphrosiderite—altered to hematite. In higher stages of oxidation martite formed from magnetite.

When minnesotaite is found oxidized, the same pattern is observed regardless of whether the resulting oxide is hematite or is goethite. Where single fibers of minnesotaite are oxidized, hematite and goethite generally are concentrated at the mid-point of the crystal and decrease in amount toward either end of the fiber. Hematite, when found in rosettes and bundles of minnesotaite, is mostly concentrated at the common center. As the fibers are traced away from this junction the oxide decreases in amount. Generally where acicular minnesotaite has penetrated siderite, minnesotaite fibers are oxidized completely, whereas the enclosing siderite is unaltered. The oxidation of minnesotaite in the presence of unoxidized siderite is common. Such a relationship is not restricted to the iron talc, for oxidized stilpnomelane and grunerite commonly show the same relative positions to unoxidized siderite. Excellent examples of all stages of the transition from partly altered to completely altered minnesotaite were obtained from the magnetite jasper horizon near Wakefield.

Stilpnomelane, oxidized to hematite, was identified in all stages from partly altered to completely altered. The oxidation of stilpnomelane follows closely that described for minnesotaite, except that the oxidation more commonly proceeds from the grain boundaries inward. The iron oxide resulting from the oxidation of stilpnomelane is either specular or micaceous hematite. Although the clear, blood-red flakes of specular hematite were recognized in transmitted light, identification was confirmed by reflected light examination. The investigation in reflected light revealed further that what was called in transmitted light, magnetite partly oxidized to martite, in many cases is unoxidized magnetite surrounded by oxidized stilpnomelane or minnesotaite.

As may be observed in the Bijiki formation at the Imperial mine, grunerite oxidizes to goethite much in the same manner as does minnesotaite. Hematite is commonly associated with goethite as an end product of the oxidation of grunerite.

Generally the alteration of aphrosiderite to hematite results in a very fine-grained specular hematite that is confined almost entirely to the boundaries of the previous aphrosiderite grain. This change must have taken place at least at the time of secondary oxidation, if not before, because the most highly oxidized aphrosiderite grains are associated with fractures filled with oxidized silicates of all types. A rock containing aphrosiderite disseminated in chert was traced into a jasper horizon at the Vicar mine; the aphrosiderite is oxidized to form the red chert of the jasper, but the magnetite is unaltered.

The oxidation of magnetite to martite (octahedral hematite) has taken place on a large scale in many localities of the eastern Marquette and eastern Gogebic ranges; martite is a common mineral in and around soft ore bodies. The investigations as to the origin of martite by Sosman and Hostetter (65)

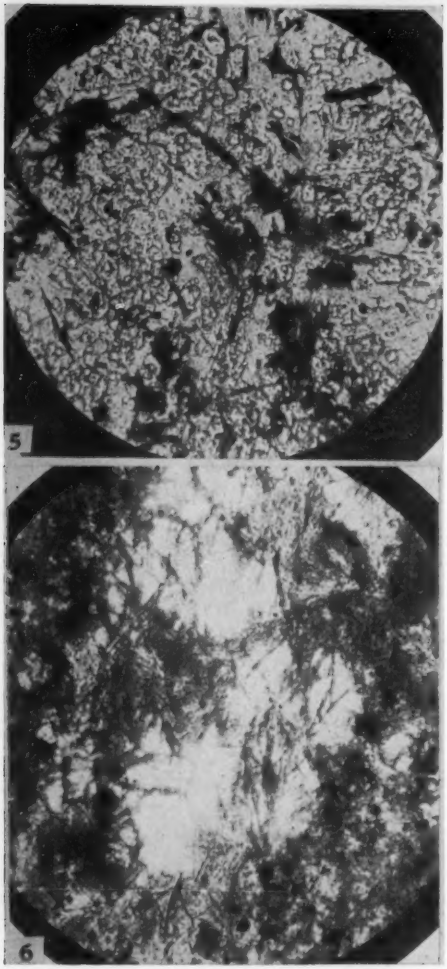


FIG. 5. Silicates oxidized in presence of unoxidized siderite. Siderite (white) veined by minnesotaite (gray) which is oxidized to hematite (black). WO analyzer, × 430, Sec. 7, T 47N, R 26W, Michigan.

FIG. 6. Silicates oxidized in presence of unoxidized siderite. Siderite (white) veined and replaced by stilpnomelane (gray) which is oxidized to hematite (black). WO analyzer, × 430, Sec. 12, T 47N, R 45W, Michigan.

and the conclusions they reached that a solid solution exists between hematite and magnetite have been discussed by many workers. Broderick (7) and later Gruner (23), concluded that the Lake Superior martites are an oxidation product from magnetite. Later Greig, Merwin, Posnjak, et al. (20, 21) synthesized martite from magnetite by oxidation in air. From this work Edwards (15) summarized criteria by which this relationship may be recognized. By following Edwards' criteria the author concluded that considerable quantities of martite had formed by oxidation of magnetite in the Negaunee and Ironwood formations.

Oxidation of magnetite to martite followed the pattern described by Gruner (22, p. 6). Hematite developed first along the octahedral planes of magnetite and spread outward until all areas between the (111) and other planes became hematite. In reflected light one observes that the octahedral form is still retained, although the martite crystal may be shattered. As in the case with magnetite there are no indications of a reaction between martite and other minerals. Martite is representative of the highest state of oxidation in the iron formation. Although partly oxidized magnetite still persists in rocks that are otherwise moderately oxidized, generally when martite is found, the iron minerals in the immediate environment are highly oxidized. Only one exception to this general statement was noted; in this case martite was identified in a zone of silication surrounded by chlorites and by minnesotaite. This relation was interpreted as a result of superimposed silication upon a formerly oxidized, unsilicated, and therefore essentially unleached rock.

Zones of martite are found in many soft ore bodies of the Marquette range, such as at the Mary Charlotte and the Tracy mines. Much of the ore of Cliff's Shaft is martite, although magnetite with iron silicates occurs near the new power plant at the eastern end of the mine. This ore body appears to have been a hard ore, in part at least, whose constituents—magnetite and iron silicates—when locally subjected to secondary oxidation, altered to martite and soft earthy hematites respectively. When a sample of Cliff's Shaft martite is dissolved and reduced by stannous chloride and hydrochloric acid, the residue is a silica gel with negative octahedrons. The low silica content of magnetite and martite indicates that they did not pass through a silicate stage. In the jaspers of the eastern Marquette range, as well as in many ores of this district, the martite-magnetite ratio is high; for example at Jasper Nob the ratio is nearly 100. In the jaspilites of the Negaunee formation in the western Marquette, such as from Michigamme westward toward Three Lakes, the martite-magnetite ratio is very low. As this ratio is the only discernible difference between the jaspilites of the two districts, it most likely represents secondary oxidation processes.

The mineral alterations and associations noted above led the present author to conclude that of the three steps in ore development suggested by Leith—oxidation, leaching, and addition of iron—the initial controlling factor was oxidation. Whereas migration of iron could not be evaluated satisfactorily, leaching without oxidation was not recognized. In the Negaunee and Ironwood formations the soft ores are confined to areas of oxidation; thus all the ores are oxidized, but not all oxidized formations are ore. Many fer-

ruginous cherts and jaspers are as highly oxidized as are their associated ore bodies; they are not ore because of their high silica content. These cherts all possess a common feature—they were only partly silicated. The silica which remains is still in the form of unleached chert. Thus, silication, which tends

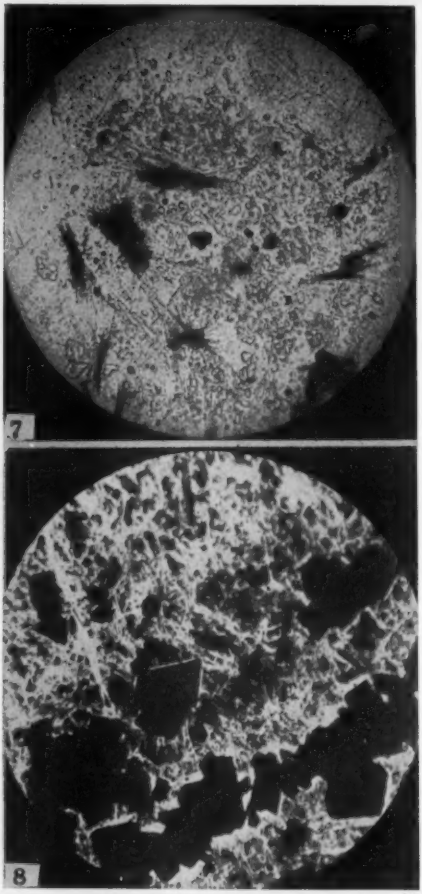


FIG. 7. Silicates oxidized in presence of unoxidized siderite. Siderite (white) dissected by fibrous minnesotaite which is oxidized to hematite (black). WO analyzer, × 430, Sec. 12, T 47N, R 45W, Michigan.

FIG. 8. Silicates and magnetite. Stilpnomelane (gray) altered to hematite (dark gray) in presence of unaltered magnetite (black). WO analyzer, × 430, Sec. 12, T 47N, R 45W, Michigan.

to facilitate chert removal, must have exerted a controlling influence on the ore process. If leaching was a unique process it should have affected all facies in a manner such as did oxidation; however only oxidized formation has suffered leaching of silica. Leached, unoxidized iron formation has not been reported in the Negaunee and Ironwood formations. If a fluid, capable of oxidizing the iron minerals and leaching silica readily from silicates—but more slowly from chert—affected an irregularly and gradationally silicated iron formation for different periods of time, the pattern of oxidation and ore would be the same as that observed in the Marquette and Gogebic ranges today.

Although no singular fluid could have remained unchanged in traversing the iron formation, the general uniformity of ores which caused Van Hise and Leith (70, p. 243) to compare the soft ores of the Marquette district with those of the Gogebic district, testifies that certain general features of the solutions may be established within limits. Such hydrous solutions—oxidizing the ferrous iron and capable of dissolving silica from silicates—locally must have been high in carbon dioxide, because considerable quantities of siderite were lost before and during oxidation. Furthermore the fluids could have been no stronger acid than a concentrated carbonic acid solution, for in low stages of oxidation, siderite and magnetite are unoxidized in the presence of oxidized silicates. All gradations were observed from this low stage of essentially unleached, but partly oxidized formation, to highly oxidized iron formation where iron is represented only by martite and fine-grained hematites. Such a transitional pattern indicates that the iron-bearing minerals were altered by a weakly oxidizing solution that was capable of completely oxidizing magnetite to martite only if allowed sufficient time.

By correlating the petrographic study of mineral alterations with field relations recorded by Tyler (66), the present author concludes that the fundamental differences between soft ores and ferruginous cherts—as well as local variations of each group—are a result of the amount and degree of metamorphism and the length of time of reaction of the oxidizing solutions.

### MINOR MINERALS OF THE IRON FORMATION AND THEIR ALTERATIONS.

*Introduction.*—Further information as to the nature of the oxidizing solutions may be obtained from a study of the chemistry of the alterations of minor minerals affected by oxidation. All compounds must have attempted to establish equilibrium with the attacking solutions, and therefore the resulting minerals should be indicative of the process of oxidation. Although some of the changes may be recognized by means of minerals, in many cases, the minerals are so fine grained that the alterations can be determined only by chemical analyses.

*Minerals and Elements and Their Reaction to the Ore Process.*—Pyrite occurs commonly in all facies of the iron formation as fracture fillings associated with basic dikes. Whereas locally—in the Athens mine in the Marquette range or in the Presque Isle mine in the Gogebic range—quartz and pyrite veins are abundant in soft ore, there is no evidence that sulphur was an

oxidizing agent in the ore process. Commonly pyrite occurs in veins around which there is no associated oxidation; however, pyrite veins may possess highly oxidized walls that continue far beyond the point where pyrite terminates. Thus, although sulphur cannot be considered the oxidizing agent, the same channels which were open to pyrite were also open to the earlier oxidizing solutions. If the source of pyrite was hydrothermal, it is likely that the source of the oxidizing solutions was also hydrothermal.

Manganese could not have been the major oxidizing agent even though its ions are capable of oxidizing ferrous iron. Rhodochrosite was identified by Seaman (64, p. 28) in unaltered iron formation, but in oxidized formation manganite, pyrolusite, or psilomelane are the common minerals bearing this element. Thus, manganese, which would have been reduced if it were the oxidizing agent, was oxidized by the ore-forming solutions.

Tyler has tabulated the actual, as well as relative changes in iron, silica, and alumina in the process of oxidation of a chloritized basic dike. He concluded: "This type of alteration is certainly not characteristic of surface weathering. . . ." The results of additional analyses of these same samples for titanium further emphasized Tyler's conclusions, because titanium oxide is lost in tremendous quantities relative to iron during oxidation. The measured quantities as well as the calculated ratios are presented in the table below. This table is identical in sequence as well as nomenclature to Table 2, offered by Tyler (66, p. 1122).

ANALYSES OF FRESH AND ALTERED CHLORITIZED DIKES.

| | Fe | $TiO_2$ | $TiO_2$/Fe |
|---|---|---|---|
| 1. Fresh | 27.05 | 2.36 | .0872 |
| Altered | 58.79 | .18 | .0031 |
| 2. Fresh | 28.95 | 2.44 | .0843 |
| Altered | 56.99 | .13 | .0023 |
| 3. Fresh | 27.73 | 1.99 | .0717 |
| Altered | 55.31 | .14 | .0025 |
| 4. Fresh | 23.10 | 2.08 | .0090 |
| Part. Alt. | 42.96 | .62 | .0014 |
| Hi. Alt. | 62.66 | .10 | .0016 |

Phosphorus is a widespread, but minor, element in the iron formations. Whereas apatite has been recognized as an original mineral in the siderite-cherts, no phosphorus-bearing mineral has been identified in soft ores; however, chemical analyses indicate that at least two phosphorus-bearing minerals occur in ore, because only part of the phosphorus is acid soluble (William Pasich: oral comm.). In the Negaunee and Ironwood formations the ratio of phosphorus to iron in the soft ores, though variable, is found to be equal to, or greater than the ratio of P/Fe in the original rock. The average analyses

offered by Mead (70, p. 247) for the rock types of the Gogebic range perhaps are tyical for both ranges.

| Rock | P/Fe |
|---|---|
| Cherty iron carbonates | .001060 |
| Ferruginous chert | .001600 |
| Iron ore | .001067 |

From this he concluded "Examination of the average analyses of the cherty iron carbonates, ferruginous cherts, and ore shows that the ratio of phosphorus to iron has remained practically constant during the concentration of the ores; in other words, both have been concentrated to essentially the same degree."

Mead also suggested that locally high phosphorus ores were a consequence of the chemical composition of the dikes, for he stated (70, p. 249): "High phosphorus ores commonly occur immediately above or below dikes. The dikes themselves are characteristically high in phosphorus, and, furthermore, the alteration of the dike is accompanied by a loss of phosphorus. It is possible that the high phosphorus in the neighboring ore may be contributed by the altering dike rock."

An examination of the detailed chemical analyses of the alteration by oxidation of a basic dike to paint rock on the same range, which Mead (70, p. 245) offered as typical for such a rock change, shows that phosphorus is actually increased relative to iron. The ratio of $P_2O_5$/Fe which was .0142 in the original rock increased to .0446 in the altered facies; in the recalculated altered facies, which assumed alumina constant, the ratio was .0445—essentially the same as before it was recalculated. Furthermore, if the recalculated analyses are compared with those of the fresh rock, it may be observed that only 15 percent of the original $P_2O_5$ was lost from the dike during oxidation.

The manner in which phosphorus and iron behaved in soft ore development in the Negaunee and Ironwood formations is different from the way they react to known weathering processes. Most analyses published as examples of weathering of basic igneous rock—such as those presented by Merrill (55, p. 225), Clarke (12, p. 464), and Goldich (19, p. 42), show a decrease in the P/Fe ratio as alteration progresses. The detailed analyses of the development of a laterite by weathering of a serpentine presented by Leith and Mead (70, 47) show clearly that, except at the immediate surface, the ratio of P/Fe has decreased noticeably from what it was in the original rock; only from the surface to a depth of 6 feet was the ratio higher than that in the original rock. Averaged analyses of distinct zones as listed by Leith and Mead (47) are:

| Depth from surface | Rock | P/Fe |
|---|---|---|
| 0–6 feet | Iron ore | .000374 |
| 6–28 feet | Iron ore | .000101 |
| 28–29 feet | Serpentine | .000141 |

If the Cuban laterites and the Michigan soft iron ores have originated as a consequence of the same processes as Van Hise and Leith (70, p. 540) imply, then both should exhibit the same pattern in the P/Fe ratio; they do not. In

weathering, phosphorus is decreased relative to iron; in the processes that developed soft iron ores in Michigan, phosphorus is increased relative to iron. Furthermore, the sharp phosphorus cut-off at depth in laterite ores known to have formed by weathering is not evident in the soft ores of the Negaunee or Ironwood formations. As the same solutions that oxidized the iron formations to ore also increased the P/Fe ratio, and an increase in this ratio is not indicative of weathering, it is unlikely that the soft ores of the Negaunee and Ironwood formations were formed by weathering; rather it is more likely that they were formed by hypogene solutions.

*Basic Igneous Rocks.*—A study of the alteration of basic igneous rocks in the iron formations, from a mineralogical point of view, offers additional information regarding the type of solutions that were active during ore development. Many basic rocks—intrusive as well as extrusives—are found in the iron formations; only rarely are they unaltered. When chloritized these rocks generally are called greenstones, but when the altered rock is white and slippery it is called soapstone. Van Hise and Bayley (69, p. 510–512) recognized that the general term soapstone included at least three distinct rocks consisting of either talc, kaolinite, or sericite. Paint rock, another miners' term, is any of the three white rocks that it stained by ferric oxides.

Both greenstones and soapstones are found in and associated with soft ores, and therefore they were involved in, or were a result of, the ore process. As a consequence of ore development some greenstones have been altered to ore, but under other ore-forming conditions some greenstones have been altered to soapstones. Chloritization and sericitization long have been recognized by Bateman (6, p. 89, p. 103–5) and other geologists as hydrothermal processes; furthermore, the other two minerals common to soapstone—talc and kaolinite—are recognized in deposits altered by hydrothermal activity, and with talc derived as a consequence of the activity. Bateman summarized the conclusions of the many workers who have studied these minerals and their origin. Concerning talc, Bateman (6, p. 296) stated: "It results from mild hydrothermal metamorphism perhaps aided by simple dynamic metamorphism, but never from weathering." Bateman defined kaolinite (6, p. 685): "Kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), a common product of weathering and rarely hydrothermal action." However Sales and Meyer (63) concluded that kaolinite, below the zone of oxidation in the wall-rock alteration at Butte, was due to hydrothermal activity.

Thus, of the four minerals common to the igneous rocks altered by the ore process, three are indicative of hydrothermal activity, and the other is formed in hydrothermal zones. Regardless of whether these minerals were developed prior to oxidation, or whether they originated as a consequence of the process itself, the fact that they exist in ore must indicate that they were at least partly stable in the ore-forming solutions. Furthermore, talc and sericite indicate that the altering solutions must have carried alkalis and alkaline-earths. As the original basic igneous rocks show that moderate amounts of these chemicals once were present, and now only magnesium and potassium remains, the elements must have been removed and transported by solutions that eventually approached equilibrium with the soapstones. As a

consequence the solutions must have carried both alkalies and alkaline-earths. Because these same basic solutions that hydrothermally altered the dike rocks —or approached equilibrium with the hydrothermally altered products—also produced soft ores, the soft ores of the Marquette and Gogebic ranges must have been developed by hydrothermal processes.

*Other Alterations.*—On the eastern Gogebic range in Section 8, T 47-R 44, Keweenawan flows overlie unoxidized iron formation with an angular unconformity. Thus, the iron formation was exposed to pre-Keweenawan weathering, but there is no indication that it was oxidized during the period of exposure.

Other minerals have been noted in the iron formation—some of them in ore—however their significance in the ore process is not fully appreciated or understood as yet. For example, some mines in the eastern Marquette range contain gypsum. The gypsum generally is concentrated near the top of the soft ores and decreases in amount with depth to where a sharp cut-off is encountered. At the South Jackson pit near Negaunee, Michigan, gypsum, barite, and manganite occur in the proximity of a large greenstone dike. Nontronite was observed by Ayres (5, p. 433) in the New Richmond mine of the Marquette range, but its full significant was not evaluated. A list of the other minor minerals and elements noted by Snelgrove (64) in the Negaunee formation includes pyroxene, amphiboles, garnets, chloritoid, tourmaline, galena, sphalerite, cadmium, malachite, chalcopyrite, gold, silver, and nickel. Chromium-bearing micas were reported by Rominger (61, p. 136), and euclase was identified by Crump (13) in the Edwards mine. None of these minerals have been found in the Negaunee or Ironwood formations in sufficient concentration to have played a signficant role in the development of the soft ores.

*Summary of Alteration of Minor Minerals.*—The ore-forming process as expressed by minor minerals in the iron formation as well as mineral transitions in associated rocks may be explained most readily by hydrothermal activity; in fact some are to be explained only on the basis of hydrothermal solutions. Furthermore, the alterations indicate that the effective solutions were high in alkali and alkaline-earths, and that the major oxidizing agent most likely was not managanese, chromium, chlorine, or sulphur. Therefore, as a consequence of all mineral alterations only three fluids—oxygen, water, and carbon dioxide —could have been abundant enough in the iron formation during ore development to have been the oxidizing agent; however, mere abundance is not enough to establish any fluid as the oxidizing agent. The energy states of each must first be evaluated to see if it is capable of the oxidation of ferrous iron to the various forms of hematite.

## THERMODYNAMICS.

*Introduction.*—The evaluation of carbon dioxide and water as oxidizing agents to ferrous iron compounds was carried out by the present author according to the principles of thermodynamics (60, 18). There is no need of evaluating oxygen because it unquestionably is capable of the oxidation.

The mineralogical transformations are a response to physical and chemical

changes in conditions; they represent a change in energy that must have been supplied either from within or without the individual system. Even though thermodynamics considers a closed system—a highly improbable situation in geological processes—some sound geological information may be obtained from the study of such a system. By isolating a system under specific conditions one may ascertain whether or not the system is capable of supplying sufficient energy to carry out the reaction. If it is thermodynamically possible, an appeal to other agents is unnecessary.

There are many ways in which to express the changes of energy in a reaction; one is by means of free energy ($dF$), and another is by the equilibrium constant obtained from partial pressures ($K_p$). Absolute free energy is often unknown, but changes in free energy may be measured. The change in free energy provides a measure of the extent to which substances may unite chemically. A simple relation exists between $K_p$ and $dF$, and once one is found the other may be calculated. In heterogeneous equilibrium, an equilibrium constant of the fluid phase is readily obtainable. Because the reactions under consideration are heterogeneous—solids and fluids—they are reported in terms of equilibrium constants. A positive constant—or negative $dF$—implies that the reaction so arranged is capable of proceeding in the direction assigned without addition of external energy.

*Alterations.*—The transitions of the solids considered were all of oxides of iron; they are ferrous oxide to magnetite, ferrous oxide to hematite, and magnetite to hematite. Free energies of the silicates and carbonates of iron are not available. The energy of decomposition of the silicates, thus may be enormous or inconsequential; as yet there is no way of evaluating that energy.

The free energies of these individual oxides have been the subject of considerable research by many chemists (54). The most widely used values are those compiled by Ralston (58); however as a consequence of work by Austin (3), Chipman and Murphy (11) were able to present information for a better set of free energy values for these compounds. The values used in this report are from the data of Chipman and Murphy.

The oxides of iron were evaluated at various temperatures in the presence of water and carbon dioxide. Values used for these fluid reactants and products are those offered by Wagman et al. (76). With carbon dioxide as the agent, transitions in the oxides are dependent upon the dissociation temperature of carbonates. For siderite Krustinson (42) found the vapor pressure of carbon dioxide to be 760 mm of mercury at 282° C, but the sample he used for this determination had impurities which indicate that his value might be slightly high. According to Harker (33, p. 77), pure magnesium carbonate has a dissociation temperature of 402° C, and calcite dissociates at 898° C. The dissociation temperature for rhodochrosite was found by Krustinson (43) to be 407° C. Thus the dissociation temperature of siderite is the lowest of the common carbonates.

Transitions of the iron oxides in the presence of carbon dioxide have been of considerable geological interest since Butler (9) first suggested that some hematites might have been produced in this manner. Lasky (44) showed that such a reaction was thermodynamically improbable because of insufficient sup-

ply of carbon to drive the reaction. More recently Roberts and Bartley (59) reapplied Butler's hypothesis to the origin of Steep Rock Lake, Ontario, iron deposits. This application was reviewed by Hawley and Robinson (34) who found that the oxidation was improbable for the same reasons offered by Lasky. The conclusions reached by the present author in this investigation regarding the oxidizing nature and ability of carbon dioxide are in agreement with those of Hawley and Robinson. The quantity of carbon dioxide necessary to transform ferrous oxide formed by the dissociation of ferrous carbonate into hematite must be far greater than that released by the dissociation. Furthermore there is a much stronger tendency to form magnetite under such conditions.

The relations of the iron oxides to one another in the presence of water at various temperatures also have been the concern of many investigators since Chaudron (54, p. 365). Portions of this study have been presented by Eastman and Evans (14), Emmett and Schultz (16), and more recently by Austin and Day (4). Gruner (25, p. 713) proposed that steam was capable of oxidizing magnetite, and he performed laboratory experiments showing that this was possible to temperatures as low as 250° C. These experiments were repeated by the present author, and extended down to 180° C. According to thermodynamics there is no reason why this reaction could not be carried to even lower temperatures. As noted in the tables below, this reaction is in opposition to the direction of the arrow—it must be driven. Such a reaction may be driven if two conditions are satisfied; 1. there must be an abundance of water, and 2. the product, hydrogen, must be removed from the reaction. In nature both of these conditions could be satisfied easily. The reactions and their equilibrium constants are as follows:

1. $2FeO + CO_2 \rightarrow Fe_2O_3 + CO : K_1 = CO/CO_2$
2. $3FeO + CO_2 \rightarrow Fe_3O_4 + CO : K_2 = CO/CO_2$
3. $2Fe_3O_4 + CO_2 \rightarrow 3Fe_2O_3 + CO : K_3 = CO/CO_2$
4. $2FeO + H_2O \rightarrow Fe_2O_3 + H_2 : K_4 = H_2/H_2O$
5. $3FeO + H_2O \rightarrow Fe_3O_4 + H_2 : K_5 = H_2/H_2O$
6. $2Fe_3O_4 + H_2O \rightarrow 3Fe_2O_3 + H_2 : K_6 = H_2/H_2O$

| T° K | $K_1$ | $K_2$ | $K_3$ | $K_4$ | $K_5$ | $K_6$ | T° C |
|---|---|---|---|---|---|---|---|
| 400 | $1.04\times10^{-2}$ | 15.12 | $4.4\times10^{-9}$ | 14.25 | $9.3\times10^{4}$ | $6.5\times10^{-6}$ | 127 |
| 500 | $1.04\times10^{-2}$ | 12.61 | $1.1\times10^{-8}$ | 1.21 | $1.3\times10^{3}$ | $1.5\times10^{-6}$ | 227 |
| 600 | $1.06\times10^{-2}$ | 3.32 | $1.3\times10^{-7}$ | .39 | $8.9\times10$ | $3.5\times10^{-6}$ | 327 |
| 700 | $1.11\times10^{-2}$ | 1.52 | $3.1\times10^{-6}$ | . | $1.4\times10$ | $2.8\times10^{-5}$ | 427 |
| 800 | $1.17\times10^{-2}$ | .12 | $1.3\times10^{-4}$ | . | 3.7 | $5.5\times10^{-5}$ | 527 |
| 900 | $1.23\times10^{-2}$ | .15 | $8.7\times10^{-5}$ | . | 1.4 | $1.9\times10^{-4}$ | 627 |

Thus the table indicates that magnetite can form spontaneously from ferrous oxide in the presence of water up to 900° K; with carbon dioxide as the reagent magnetite will form at temperatures up to 700° K. Although there is a tendency for hematite to form from ferrous oxide in the presence of water

vapor at lower temperatures, there is more of a tendency for the development of magnetite, as evidenced by the high positive values of $K_5$ compared with the slightly positive values of $K_4$. In order for the reactions to proceed in the direction of the arrows all the reactions which are negative (less than 1), values must be driven by an excess of fluid. Hence no appreciable quantity of hematite will form from ferrous oxide unless it is acted upon by an excess of $CO_2$; at the same time there is even a stronger tendency to develop magnetite. Once magnetite is formed only a tremendous excess of fluid would drive magnetite to martite. With $CO_2$ as the fluid at 700° K, an excess of $10^7$ parts of $CO_2/CO$ would be necessary to drive the reaction—provided CO is removed. Such an excess during the oxidation is highly unlikely, unless some external hypogene source of $CO_2$ is called upon. With water as the reactant, an excess of $10^7$ ($H_2O/H_2$) is probable from hypogene sources as well as from supergene sources. In addition, water acting for a long period of time is most capable of dissolving silica from the relatively soluble iron silicates.

It should be mentioned that these thermodynamic calculations consider only water, carbon dioxide, carbon monoxide, and hydrogen; they do not evaluate the "water-gas," or "methane" reactions which might be applicable.

On the basis of thermodynamics, the present author concludes that in an open system, with an abundant supply, water is geologically capable of oxidizing iron to hematite, either directly from ferrous oxide or through magnetite, as well as removing silica from iron silicates.

## SUMMARY AND CONCLUSIONS.

The mineral alterations and chemical changes in soft ore development in the Marquette and Gogebic ranges are not common to weathering, and for the most part are not explained by weathering. Whereas most of the alterations may be explained by hydrothermal activity, specific alterations of dikes during oxidation, are explained only by hydrothermal activity. The type of fluid found capable of oxidation of the iron formation—the first important step in soft ore development—is a hot, neutral to basic, hydrous solution, which at one time or another carried both alkalis and alkaline-earths. Available oxygen, which may or may not have been present, merely would have speeded oxidation in specific cases.

Thus the soft ores of the Negaunee and Ironwood iron formations must have originated by the action of hot hydrous solutions on silicated iron formation in the manner suggested by Gruner's modified hydrothermal theory.

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# A FIELD METHOD FOR THE DETERMINATION OF TITANIUM IN ROCKS [1]

LEONARD SHAPIRO AND W. W. BRANNOCK.

ABSTRACT.

About 4 mg of rock powder measured with a scoop is fused with potassium bisulfate in a test tube. Tiron is added to the cool melt and the mixture is dissolved in a buffer solution. Sodium dithionite is added and the approximate concentration of $TiO_2$ is determined by comparing the resulting yellow solution with permanent standards, which are simple to prepare.

The results obtained by this field method for $TiO_2$ on 72 rock samples of various types are compared with those obtained by laboratory methods.

## INTRODUCTION.

THE simple field test described was originally devised for use by geologists in the field as a tool to aid in the correlation studies of certain iron and slate formations in the Cuyuna iron district in Minnesota.

By this method it is easy for a person, with meager experience in chemical analysis and with simple and inexpensive apparatus, to differentiate rocks containing 0, 0.5, 1, and 2 percent titanium oxide. Rocks with higher concentrations of the oxide can be differentiated by appropriate dilution of the colored solutions used in the test.

The procedure is an adaptation of a method by Yoe and Armstrong [2] based on the yellow color produced by the reaction of titanium with tiron (disodium-1, 2-dihydroxybenzene-3, 5-disulfonate). The effect of iron, which forms a purple solution with tiron, is eliminated by reduction with sodium dithionite.

## REAGENTS.

Potassium bisulfate ($KHSO_4$), fused powder.

Tiron (disodium-1, 2-dihydroxybenzene-3, 5-disulfonate), the dry reagent powder.

Buffer solution, 40 g of ammonium acetate and 15 ml of glacial acetic acid made to 1 liter volume with distilled water.

Sodium dithionite ($Na_2S_2O_4$) (sold as sodium hydrosulfite), the dry reagent powder.

Potassium dichromate ($K_2Cr_2O_7$).

[1] Publication authorized by the Director, U. S. Geological Survey.

[2] Yoe, John H., and Armstrong, Alfred R., Colorimetric determination of titanium with disodium-1, 2-dihydroxybenzene-3, 5-disulfonate: Analytical Chemistry, vol. 19, pp. 100–102, 1947.

### APPARATUS.

Test tubes for fusions and color comparisons, 18 × 150 mm pyrex, marked with a stylus at the 15-ml volume level. At least 12 tubes are desirable; 4 are necessary.

Graduated cylinder, 25 ml.

Sample scoop. A strip of metal 1/8 × 3/16 × 7 in. with a hole 1/16 in. in diameter and 1/16 in. in depth drilled near one end.

Reagent scoop. A strip of metal 3/8 × 3/8 × 4 in. with a hole 7/32 in. in diameter and 1/4 in. in depth drilled near one end.

Spatula, small.

Plattner mortar for crushing rock samples. Mortar with pestle diameter of 20 to 25 mm.

Blowtorch, Bunsen burner, or other source of heat with sufficient capacity to heat a test tube to red heat.

Mortar and pestle for powdering samples. Conventional mortar and pestle of hard material such as agate, mullite, or porcelain. Mortar diameter should be about 65 mm.

Hammer, for breaking large pieces of rock down to size suitable for crushing in Plattner mortar.

### PREPARATION OF STANDARDS.

It is advisable for convenience to prepare and use a series of permanent color-comparison standards. Colored solutions formed by the reaction of titanium with tiron, as described below under "Procedure," are not practical for use as permanent standards because upon standing for a few minutes after color development, they become cloudy as the result of precipitation of sulfur. Satisfactory permanent standards can be prepared from potassium dichromate solutions by adjusting the concentration of a dichromate solution to match the color intensity of a solution prepared as described below under "Procedure" from a sample powder of known $TiO_2$ concentration.

In order to eliminate more nearly chance error in the preparation of the standards, the color should be developed for three separate portions of the sample of known $TiO_2$ concentration and the initial permanent dichromate standard solution should be made to match the color of the solution with the median color intensity.

National Bureau of Standards standard clay sample No. 97, in which the $TiO_2$ concentration is 2.38 percent, can be used conveniently for preparation of a standard solution equivalent to 2 percent $TiO_2$ in a sample by making the final solution volumes to 18 ml instead of 15 ml as described under "Procedure." The standard solutions are prepared as follows:

1. Place about 100 mg of National Bureau of Standards standard sample No. 97 on a small piece of clean paper, resting on a smooth flat surface, and press the sample scoop several times into the powder until the hole is filled. Wipe off the excess powder so that the powder in the hole is level.
2. Tap the powder into one of the test tubes.
3. Measure two additional sample portions by repeating steps 1 and 2 two times.

4. Add a scoopful (reagent scoop) of potassium bisulfate to each test tube.
5. Heat each test tube in a hot flame until the flux has been molten and fluid for 1 to 2 minutes.
6. After the test tubes cool add about a scoopful (reagent scoop) of tiron to each test tube.
7. Add 18 ml of buffer solution to each tube and gently heat until the fused cakes dissolve.
8. Allow the solutions to cool on standing, or cool to air temperature in cool water.
9. Add several mg of sodium dithionite to each tube, with a spatula. Cap with the thumb and invert each tube once.
10. Dilute a solution of potassium dichromate (at least 50 ml) with water until, when transferred to a test tube, the color matches the color of the solution of median intensity obtained in step 9.
11. Transfer 15 ml of the dichromate solution from step 10 to a test tube. Stopper or seal and retain as a permanent standard equivalent to 2% $TiO_2$ in a sample.
12. Mix 25 ml of the dichromate solution from step 10, equivalent to 2% $TiO_2$, with 25 ml of distilled water.
13. Transfer 15 ml of the dicromate solution from step 12 to a test tube. Stopper or seal and retain as a permanent standard equivalent to 1% $TiO_2$ in a sample.
14. Mix 25 ml of the dichromate solution equivalent to 1% $TiO_2$ with 25 ml of distilled water.
15. Transfer 15 ml of the dichromate solution from step 14 to a test tube. Stopper or seal and retain as a permanent standard equivalent to 0.5% $TiO_2$.

## PROCEDURE.

1. Prepare about 50 mg of finely powdered sample, representative of the total sample, by crushing, grinding, and quartering the original sample with a hammer, Plattner mortar, and conventional mortar and pestle.
2. Place the sample powder on a small piece of clean paper resting on a smooth flat surface and press the sample scoop several times into the powder until the hole in the scoop is filled. Wipe off the excess sample powder with the finger so that the powder in the hole is level.
3. Tap the powder into the bottom of one of the test tubes.
4. Add a scoopful (reagent scoop) of potassium bisulfate.
5. Heat the test tube in a hot flame until the flux has been molten and fluid for 1 to 2 minutes.
6. After the test tube cools add a scoopful (reagent scoop) of tiron.

**TABLE 1.**

REPRODUCIBILITY OF SAMPLE SIZES MEASURED WITH SCOOP (IN MG).

| Clay | Granite | Diabase | Iron ore | Iron ore |
|---|---|---|---|---|
| 4.2 | 4.2 | 4.3 | 5.6 | 7.3 |
| 4.2 | 4.1 | 4.1 | 5.6 | 6.8 |
| 2.8 | 4.1 | 4.2 | 5.5 | 6.8 |
| 4.2 | 4.0 | 4.4 | 5.6 | 6.9 |
| 4.0 | 4.0 | 4.3 | 5.6 | 4.7 |
| 4.0 | 4.0 | 4.1 | 5.9 | 7.1 |

TABLE 2.

DETERMINATION OF $TiO_2$ IN ROCKS.

| Sample No. | Type of rock | Percent $TiO_2$ | |
|---|---|---|---|
| | | Laboratory method | Field method |
| | Cuyuna District, Crow Wing County, Minnesota | | |
| 1 | Iron formation | 0.07 | Nil |
| 2 | do. | 0.05 | Nil |
| 3 | do. | 0.07 | 0.1 |
| 4 | do. | 0.11 | 0.1 |
| 5 | do. | 0.07 | Nil |
| 6 | do. | 0.10 | Nil |
| 7 | do. | 0.13 | Nil |
| 8 | do. | 0.05 | Nil |
| 9 | Slate | 1.8 | 2 |
| 10 | do. | 0.55 | 0 5 |
| 11 | do. | 0.48 | 0.5 |
| 12 | do. | 2.5 | 2 |
| 13 | do. | 2.3 | 2+ |
| 14 | do. | 2.3 | 2 |
| 15 | do. | 0.44 | 0.3* |
| 16 | do. | 0.79 | 0.5* |
| 17 | do. | 1.9 | 1.5* |
| 18 | do. | 0.85 | 0.9* |
| 19 | do. | 0.43 | 0.2* |
| 20 | do. | 1.9 | 1.7* |
| 21 | do. | 0.71 | 0.6* |
| 22 | do. | 0.19 | 0.1* |
| 23 | do. | 0.12 | Nil* |
| | Arizona | | |
| 24 | Altered quartz monzonite | 0.37 | 0.5 |
| 25 | Quartz monzonite | 0.46 | 0.7 |
| 26 | Altered quartz monzonite | 0.32 | 0.4 |
| | California | | |
| 27 | Quartz porphyry | 0.18 | 0.3 |
| 28 | Quartz diorite | 0.26 | 0.3 |
| 29 | Granodiorite | 0.60 | 0.7 |
| 30 | Silicified quartz diorite | 0.25 | 0.2 |
| 31 | do. | 0.25 | 0.2 |
| 32 | Quartz diorite | 0.28 | 0.3 |
| 33 | Lamprophyre dike | 2.9 | 2.5 |
| 34 | Syenite | 0.86 | 0.5 |
| 35 | Andesite dike | 1.0 | 0.7 |
| 36 | Granite | 0.32 | 0.2 |
| 37 | Shonkinite | 1.6 | 1.3 |
| 38 | do. | 2.2 | 1.5 |

* Determinations made in the field by R. G. Schmidt, U. S. Geological Survey.

TABLE 2.—*Continued.*

| Sample No. | Type of rock | Percent $TiO_2$ | |
|---|---|---|---|
| | | Laboratory method | Field method |
| | **Maine** | | |
| 39 | Rhyolite | 0.34 | 0.3 |
| 40 | Andesite | 0.78 | 0.7 |
| 41 | do. | 0.80 | 0.7 |
| 42 | Spilite | 3.3 | 3+ |
| 43 | do. | 2.6 | 2+ |
| 44 | Andesitic volcanic | 1.6 | 1.8 |
| 45 | Spilite | 0.40 | 0.2 |
| 46 | Metabasalt | 0.90 | 1.0 |
| 47 | do. | 0.86 | 1.0 |
| | **Nevada** | | |
| 48 | Kaolinite-alunite | 0.28 | 0.1 |
| 49 | Calcite | 0.08 | Nil |
| 50 | Granodiorite | 0.55 | 0.7 |
| 51 | Andesite | 0.71 | 0.7 |
| 52 | Granodiorite | 0.83 | 0.6 |
| | **Aleutian Islands** | | |
| 53 | Basalt porphyry | 0.74 | 0.7 |
| 54 | Basalt | 0.88 | 0.8 |
| 55 | Andesite | 0.66 | 0.6 |
| 56 | Diabase | 2.0 | 1.5 |
| 57 | Altered diabase | 1.8 | 1.5 |
| 58 | Basaltic lava | 0.99 | 1.2 |
| 59 | Albitized lava | 0.86 | 0.8 |
| 60 | Diabase dike | 1.3 | 1.3 |
| 61 | Recrystallized palagonitic tuff | 1.0 | 1.0 |
| 62 | Normal palagonitic tuff | 1.2 | 1.2 |
| 63 | Granophyre | 0.18 | 0.2 |
| 64 | Olivine basalt | 0.51 | 0.3 |
| 65 | Vitreous andesite | 0.81 | 0.3 |
| 66 | Dacite pumice lapilli | 0.64 | 0.2 |
| 67 | Andesite | 0.93 | 0.7 |
| 68 | Andesitic tuff | 1.2 | 0.6 |
| 69 | Quartz keratophyre | 0.75 | 0.6 |
| 70 | Latite | 0.82 | 0.4 |
| 71 | Vitreous andesite | 1.0 | 0.1 |
| 72 | Argillite | 0.72 | 0.7 |

7. Add 15 ml of buffer solution and gently heat until the fused cake dissolves.
8. Allow the solution to cool to air temperature or cool by dipping the test tube in cool water.
9. Add several mg of sodium dithionite with a spatula, cap the test tube with the finger and invert once.
10. After 1 minute compare the color with that of the standards to estimate the concentration of $TiO_2$ in the sample.

## EXPERIMENTAL RESULTS.

To determine the feasibility of using the small metal scoop for measuring sample portions, six portions of each of five sample powders were measured and weighed. The results obtained are shown in Table 1. The values for each sample powder are in good agreement except for the 2.8 for the clay and the 4.7 for one of the iron ore samples. Such erratic values may occur occasionally, owing to incomplete filling of the scoop. The high sample weights obtained for the two iron ores are due to the relatively high specific gravities of the materials.

For materials containing relatively high $TiO_2$ concentration and having specific gravities that differ appreciably from the specific gravity of the sample used for preparation of the standard solutions, corrections can be applied for errors due to the specific gravity differences, or a sample powder of suitable specific gravity and $TiO_2$ concentration can be used for preparation of the standard solutions. For normal material relatively low in $TiO_2$ the difference in specific gravity between standard and samples is inconsequential.

Table 2, samples 1 to 23, show some of the results obtained when the method was used as an aid in the correlation of certain iron and slate formations in the Cuyuna district in Minnesota. Results from the field method are compared with those from a laboratory method. $TiO_2$ was also determined by the field method in samples 24 to 72 to test the general applicability of the method to a variety of rock types from several localities, and the results obtained by the two methods are compared. The values in general are in adequate agreement. Samples 65, 66, 68, 70, and 71, for which the values are in poor agreement, are composed largely of glassy materials that are not decomposed by fusion with potassium bisulfate.

## CONCLUSIONS.

The method can be used to determine rapidly the approximate concentration of $TiO_2$ in a variety of rock types. It can not be relied upon for analysis of glassy rocks.

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# SYNTHETIC MINERALS.

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## INTRODUCTION. WHY ARE MINERALS SYNTHESIZED?

THE economically important minerals can be subdivided into three groups. The first group comprises those minerals which are mined because they provide a source of energy (anthracite, oil, radioactive elements). A second group is of economic value because the minerals contain useful elements (copper ores, pyrite, galena). Minerals of this group require processing in order to extract the useful elements. A third group comprises those minerals which are useful just as they occur in nature because they have certain desirable physical properties.

Long before the value of ores or of coal was appreciated, minerals of the third group attracted the attention of man. Some minerals were gathered and often traded over large distances. The use of obsidian for arrowheads in the Stone Age is based on the conchoidal fracture of this hard natural glass. The first minerals that attracted the attention of primitive people did so because of their color. Gold and ruby were held in great esteem because of their striking colors. Lapis lazuli (lazurite) in the form of beads was used by the ancient Greeks and has been found in the ruins of ancient Troy. Minerals played an important role in the longing of man for protection and for power. For centuries natural sciences centered around the Philosopher's Stone; this mysterious catalyst was supposed to enable its owner to change base metals into

gold. The earliest documents of the activity of man dealt with minerals, their uses and their hidden mysterious powers. Even today this relation has not disappeared completely as one can see from the custom of wearing "birthstones."

During the 18th century, chemistry and mineralogy developed into exact sciences. At this time the speculations concerning the origin of minerals were replaced by efforts to copy nature in the laboratory. When mineralogy changed from a description and a classification of minerals into an experimental science, the formation of minerals in nature was simulated by their synthesis in the laboratory. In France at the middle of the last century the first systematic efforts were made to synthesize minerals. The work of Ebelmen, Hautefeuille, Fouqué and Michel-Lévy (1)[1] marks the beginning of the synthetic era of mineralogy. The work was undertaken primarily from a scientific viewpoint, but it also produced some practical results. The devitrification, i.e., the crystallization of certain vitreous materials, led to a substance which resembled alabaster (Réaumur porcelain). The flame fusion process developed by Verneuil (2) made possible the synthesis of rubies, one of the most coveted varieties of corundum.

Today work on mineral synthesis is carried out in universities (University of Chicago; School of Mineral Industries, State College, Pa., etc.), research institutions (Geophysical Laboratory and the Naval Research Laboratory, Washington, D. C., etc.) and in industrial laboratories (Bell Telephone, Harshaw Chemical Co., Brush Development, etc.). The work in universities aims primarily at an understanding of the geological conditions under which certain minerals have formed. The synthesis of minerals is important for furthering crystal chemistry and, with it, the physics and chemistry of solids. Industrial synthesis aims at producing minerals which have desirable physical properties. Some minerals are synthesized because they are not available in required quantity in the form of large single crystals. One of the most common minerals, quartz, is plentiful in forms which are suitable for the manufacture of refractories (silica brick), for glass melting (glass sand), or for making ceramic ware (potters flint). However, for optical purposes and for certain electronic devices large and flawless single crystals are needed. In this form, quartz is relatively rare and its occurrence is restricted to a few localities (Minas Gerais, Brazil).

We shall discuss some of the synthetic minerals which are interesting from an economic viewpoint. For obvious reasons this applies only to minerals of the third group, i.e., those which have desirable physical properties.

## THE METHODS OF MINERAL SYNTHESIS.

*1. Precipitation from Solution.*—Numerous minerals can be synthesized in a finely subdivided form by bringing together, in aqueous solutions, salts which react and precipitate the less soluble compounds. The following equations describe the synthesis of calcite ($CaCO_3$), witherite ($BaCO_3$), barite ($BaSO_4$),

[1] Numbers in parentheses refer to Bibliography at end of paper.

galena (PbS), anglesite ($PbSO_4$) and crocoite ($PbCrO_4$).

$$CaCl_2 + Na_2CO_3 = 2NaCl + CaCO_3$$
$$BaCl_2 + Na_2CO_3 = 2NaCl + BaCO_3$$
$$BaCl_2 + Na_2SO_4 = 2NaCl + BaSO_4$$
$$Pb(NO_3)_2 + (NH_4)_2S = 2NH_4NO_3 + PbS$$
$$Pb(NO_3)_2 + Na_2SO_4 = 2NaNO_3 + PbSO_4$$
$$Pb(NO_3)_2 + K_2CrO_4 = 2KNO_3 + PbCrO_4$$

This method is widely used in the manufacture of pigments and numerous examples can be found in textbooks of analytical chemistry.

*2. Crystal Growth from Solutions.*—A few years ago the Faraday Society devoted a Symposium and a special volume (3) of its publications to the problems of crystal growth. It is surprising to learn that the "simple" process of NaCl crystallizing out of its aqueous solution is still surrounded by mysteries. An aqueous solution of NaCl of reagent quality allowed to stand in an open vessel crystallizes out as the water evaporates. The white dense masses consist of crystals which are not clear because they contain inclusions of mother liquor. These crystals decrepitate on heating. The same solution after "contamination" with a trace of stannous chloride or lead chloride (4) produces relatively large clear single crystals free of inclusions which melt without decrepitation.

The formation of flawless large single crystals seems to be one of nature's most closely guarded secrets. Many apparently "perfect" crystals must have formed under conditions where the proper "impurities" were available. The finest specimens of rock crystals contain traces of alkali and alumina. One is inclined to think that the diamond of gemstone quality is the purest form of carbon. Its ultraviolet absorption, however, reveals the presence of impurities (5). Carbon, which does not contain this impurity, does not form flawless crystals.

The growing of single large crystals has become an industry and an art. Some minerals are plentiful in the form of small crystals or polycrystalline aggregates but are rare in the form of large single crystals. The process of growing large crystals is time consuming. Sodium chloride and the other alkali halides can be much more easily obtained from their melt than from solutions. Other crystals like alum can be grown from aqueous solutions without serious difficulties.

Our basic knowledge of crystallization and solution processes is limited to a description of the equilibria. Solubility curves, phase equilibria diagrams, etc., provide the information on what to expect in a given system for certain temperature and pressure conditions, if one waits sufficiently long to allow the equilibrium to be established.

Rate phenomena are not as well understood as equilibrium phenomena. The factors which affect the rate of crystallization have not yet been explained in spite of their importance in crystallization processes. Minute impurities of lead chloride change the discontinuous growth of NaCl from aqueous solutions into a continuous growth, thus greatly improving the optical quality of the

crystal (6). As far as the rate of nucleation is concerned, the manufacturer of single crystals can make himself independent of this factor by seeding the solution. The large crystals of ammonium dihydrogen phosphate which are produced commercially are grown in stages. The seeding of the solutions has developed into a science (7). It is true that any piece of a crystal will grow when immersed in a supersaturated solution. However, by using sections cut in certain crystallographic direction, the time which is necessary to grow a crystal can be shortened considerably.

Only recently has it been possible to elucidate the nature of the energy barriers which control the formation of nuclei and to explain why an aqueous solution of $CaF_2$ requires a 500 per cent supersaturation in order to crystallize spontaneously, whereas those of other compounds ($PbI_2$, sulfides and halides of heavy metals) do not form metastable supersaturated solutions. The difficulty encountered in the formation of certain nuclei has its counterpart in the rate of certain compounds going into solution. A solution has to be heated for considerable time above the solubility temperature in order to dissolve completely submicroscopic crystals which would act as nuclei on cooling. These phenomena result from the increase of the specific surface energy of a crystal if its size is very small.

*3. Formation from the Melt.*—It is very difficult to obtain large crystals of NaCl from solutions. In nature rocksalt has formed from solutions over long periods of time but large and clear single crystals are relatively rare. In the laboratory it is much more convenient to produce this and related minerals, e.g., sylvite (KCl), from their melt.

The most commonly used method for growing large single crystals of salts from the melt consists of the lowering of a crucible with a conical bottom through a vertical furnace. A strong temperature gradient established in the melt causes the crystallization to commence at the bottom and to grow upwards through the melt.

The Harshaw Chemical Company has developed this method into a commercial process and produces single crystals weighing from 10 to 20 pounds and even more. These crystals, in particular NaCl, KBr, KCl, KI, LiF and $CaF_2$, are used for ultraviolet and infrared optics. Ingots of AgCl single crystals can be rolled between highly polished rolls just like metals. These AgCl sheets are used for windows and absorption cells for infrared.

Some crystals can be obtained in crucibles of pyrex glass, others have to be grown in platinum containers or in graphite molds. Minerals such as corundum or rutile have melting points which are too high for platinum, but single crystals of these high melting oxides can be produced by fusing the finely powdered material in a hydrogen–oxygen flame and spraying the droplets of the melt onto a "bait." This process is now widely used for growing single crystals: Flame Fusion Process.

*4. The Flame Fusion or Verneuil Process.*—With few minor changes the process which was developed by Verneuil (1902) is still used for producing single crystals of several varieties of corundum (ruby, sapphire, star sapphire), some spinels, rutile and some titanates. Recently scheelite, $CaWO_4$, has been obtained in the form of single crystals by the flame fusion method.

The burner which is used in the Verneuil process has an inner orifice through which is fed into the flame both oxygen and a fine powder of the compound to be used. An outer larger orifice surrounding the first one is used to feed hydrogen into the flame at a relatively low pressure. The feed material is vibrated through a screen either with a magnetic hammer or a simple mechanical tapping device. With this arrangement it is possible to grow large single crystals of those compounds (corundum, spinel) which can be melted in the hydrogen-oxygen combustion zone without decomposition. For a successful operation of the Verneuil process the control of the particle size of the feed material is extremely important; each particle has to be fused completely before it reaches the pedestal. The pedestal has to be lowered steadily at a controlled rate in order to avoid the formation of layers leading to internal stresses. Any refractory material which stands the temperature can be used as a pedestal; alumina and stabilized zirconia are most widely used. In some cases seed crystals have been used for further growth.

*5. Solid State Reactions and Phase Transformations.*—The synthesis of minerals by allowing a mixture of oxides to react in the solid state covers a wide field of simple or complex minerals such as phosphates, silicates, aluminates or ferrites. Some of the oldest pigments, iron oxides, including polishing rouge, Thénard's blue (cobalt aluminate), Rinman's green (cobalt zincate), Egyptian blue (calcium cupric silicate) and the artificial lapis lazuli (ultramarine) are produced commercially by solid state reactions. In contrast to crystallization from melts, crystals resulting from solid state reactions are usually very small, often submicroscopic. For this reason the scientific exploration of mineral synthesis on the basis of solid state reactions is relatively new. This method could not advance very far before X-rays and electron microscopes became available as the tools for following the progress of the reactions.

G. Tammann and his School as well as J. A. Hedvall (8) and his students opened up this branch of solid state chemistry at a time when many scientists still adhered to the alchemical principle *"Corpora non agunt nisi fluida."*

The experimental procedure is very simple in principle. The same method can be used for the synthesis of a ceramic pigment, of a phosphor or of a ferromagnetic spinel, namely, mixing the constituents in the proper proportions either as oxides or carbonates and heating the intimate mixture in a crucible. Complete reaction, however, is slow and depends upon the rate of diffusion. Repeated grinding, mixing and ball milling of the aqueous suspensions of the reactants may be necessary to complete the reaction.

As many properties (color, fluorescence) are a function of the size of the crystals, the heat treatment has to be carefully controlled. Frequently "fluxing agents" such as alkali salts are added to speed up recrystallization and to increase the particle size. The addition of "catalysts" plays an important role in solid state reactions.

There is a serious gap in our knowledge of the mechanism which causes the formation of minerals. We need a better understanding of rate phenomena concerning the reaction between two compounds as well as the transformation of one modification into another. A whole branch of the ceramic industry, the manufacture of silica bricks, consists of the transformation of one crystalline

phase of silica (quartz) into another (cristobalite). This process is very slow and catalysts are needed to bring this reaction close to completion. Our knowledge of the rate of this reaction as affected by catalysts is still purely empirical.

The fact that the formation of crystals is frequently dominated by rate phenomena rather than by the equilibrium makes it possible to influence them by catalysts. We cannot predict which modification of $SiO_2$ will form if silica gel or vitreous silica is allowed to crystallize. As a rule, the modification which is in equilibrium at the particular temperature does not form. Amorphous precipitated silicic acid heated to 1100°–1200° C (stability range of tridymite) forms cristobalite. It has been found, however, that in the presence of certain catalysts (CaO) crystals of quartz are formed as the first reaction product (9).

From phase equilibria we would expect that a mixture of $CaCO_3$ and $SiO_2$ in the ratio 1 : 1 would form the metasilicate, wollastonite $CaSiO_3$. However, the first product of the reaction is the orthosilicate $Ca_2SiO_4$. In order to obtain wollastonite one either has to heat the mixture for a very long time or to use a suitable catalyst. The presence of $H_2O$ vapor accelerates wollastonite formation, a method which has been used for the synthesis of wollastonite activated by manganese, a fluorescent mineral (phosphor).

*6. Reactions from the Vapor Phase.*—In connection with volcanic activities some minerals have formed from the vapor phase, either as a result of chemical reactions or by sublimation. Minerals of this type are often referred to as "pneumatolytic." J. B. Ferguson (10) showed that the reaction between CO and $SO_2$ at 1000–1200° C can lead to elemental sulfur which is found frequently as a product of volcanic activity. The synthesis of marcasite and other sulfide and arsenide minerals formed from the vapor phase were reported by A. Beutell (11).

The sublimation method is now used in the synthesis of greenockite, CdS. R. Frerichs (12) produced single crystals of CdS by allowing the vapor of metallic cadmium to react with $H_2S$ according to

$$Cd + H_2S = CdS + H_2$$

These crystals convert X-ray quanta into slow electrons so that they are used as X-ray detectors.

*7. Hydrothermal Synthesis.*—The role which water plays as a catalyst increasing the rate of formation of minerals was well established in the middle of the last century. The French synthetic school of mineralogists made the first attempts to synthesize minerals using water vapor under pressure in closed gun barrels. The early work of Daubrée and Sénarmont and the later work of Friedel and Baur is primarily of historical interest. Modern hydrothermal synthesis begins with the systematic work of G. W. Morey and his associates in the Geophysical Laboratory in Washington, D. C. In a review of the early work, G. W. Morey and E. Ingerson (13) describe the essential features of this method.

The principle of hydrothermal synthesis is relatively simple. Compounds such as $SiO_2$ and $Al_2O_3$ contain cations of high field strength which have to be surrounded by at least four anions in order to be properly screened. As a

result, the molecules $SiO_2$ and $Al_2O_3$ do not exist at normal temperatures, but polymerize and form infinitely extending three-dimensional networks. In the solid state the anions are shared between the cations so that each $Si^{4+}$ ion is surrounded by four and each $Al^{3+}$ ion by six $O^{2-}$ ions. The polymerized products, quartz and corundum, are chemically inert because they are insoluble in the usual solvents. In the presence of gaseous "mineralizers" such as $H_2O$, $Si^{4+}$ and $Al^{3+}$, the ions expanded their coordination so that the solid can depolymerize under formation of $Si^{4+}(OH)^-_4$ or $Al^{3+}(OH)^-_3$ molecules. HF and HCl have an effect which is similar to that of water; they can raise the vapor pressure of otherwise non-volatile compounds. This is strikingly illustrated by v. Wartenberg's (14) observation that $Al_2O_3$, $La_2O_3$ or BeO are non-volatile when fused in a $CO—O_2$ flame, but show considerable volatility in a hydrogen-oxygen flame. In an atmosphere of $H_2O$ these oxides even at high temperature can form hydroxides temporarily but on cooling they cleave off the water and deposit as anhydrous compounds.

Hydrothermal synthesis is a powerful tool for synthesizing those minerals which have incongruent melting points (beryl, garnet-family), i.e., minerals which cannot be obtained from the melt. In the past this method was used only in a few geochemical laboratories in order to explore Nature's secrets. During the last war, however, several occasions arose which called for the application of hydrothermal synthesis. The need for a slender rod of a fluorescent material was met by E. Ingerson and O. F. Tuttle's (15) synthesis of single crystals of willemite ($Zn_2SiO_4$) activated by manganese. This was accomplished by heating to 500°–600° C the coprecipitated hydroxides of zinc and manganese in a bomb which contained water and silica under pressures of 1,000 to 4,000 lbs./sq. in. Under these conditions the silica forms a volatile hydrate which reacts in contact with the zinc hydroxide. At the surface of the zinc compound willemite needles were formed, some of which grew 3 cm. long.

One of the most important applications of hydrothermal synthesis concerns the growth of quartz crystals. The first work on the synthesis of quartz was carried out by the French synthetic school. H. de Sénarmont (1851) and Daubrée (1857) obtained quartz from silicic acid and from the hydrolysis of glass by steam. Only microscopic crystals could be obtained by the primitive means available at this time. R. Nacken (1912) took advantage of the large difference in solubilities in diluted alkali of crystalline quartz and amorphous silica in order to grow single crystals of quartz. By using a seed crystal he devised a process where amorphous silica went into solution and quartz deposited at the seed causing a fairly rapid growth for a limited time. Quartz, feldspars, micas and beryl were obtained in small quantities by means of hydrothermal synthesis. Today the growth of quartz crystals is in a pilot plant stage and commercial production can begin whenever the need for artificial crystals becomes pressing.

## MINERALS WITH DESIRABLE OPTICAL PROPERTIES.

The use of pigments, such as chalk, yellow and red ochre, goes back to prehistoric times as can be seen from the drawings in the caves of Altamira

in Spain. With the development of ceramics and metallurgy, our oldest technologies, synthetic pigments must have been discovered as the result of the application of heat to minerals (burned ochre). At the present time mineral pigments play an important role in our economy. However, even those pigments which occur in nature such as the red and black oxides of iron, the green and blue basic carbonates of copper, the chromate of lead, etc., are now being replaced by synthetic minerals in order to obtain more uniform and reproducible products.

In contrast to the age old use of minerals as pigments, other optical properties like the birefringence of the Iceland spar, the infrared transmission of halite, and the ultraviolet transmission of quartz became of interest only in modern times with the development of scientific instruments.

*1. Synthetic Pigments.*—Many mineral pigments can be formed by precipitation from aqueous solution at ordinary or slightly elevated temperature. In some cases this method no doubt corresponds to their formation in nature. The mineral greenockite, CdS, is rather rare and of no economic significance. The synthetic product, however, represents a valuable yellow pigment which has been produced commercially by the reaction of cadmium salts in aqueous solution with hydrogen sulfide. In spite of the apparent simplicity of this reaction, it has been found necessary for some grades of this pigment to use less direct methods, e.g., forming the carbonate or oxalate first and treating these white precipitates with hydrogen sulfide. Other producers prefer to synthesize the greenockite by a dry process in which mixtures of cadmium carbonate and elemental sulfur are calcined. The latter process leads to a series of pigments ranging from pure yellow to red if selenium is substituted for a part of the sulfur. These pigments find wide applications for artist colors as well as for glasses and enamels. Some of the natural pigments, like greenockite, CdS, can be synthesized by the precipitation method. Lead chromate or crocoite, $PbCrO_4$, lead sulfate or anglesite, $PbSO_4$, the basic carbonates of copper malachite $CuCO_3 \cdot Cu(OH)_2$ and azurite, $2CuCO_3 \cdot Cu(OH)_2$, are typical examples. The color of these compounds varies with particle size and with the crystal structure. For this reason the methods of manufacture have to be closely controlled and the precise formulation is frequently guarded as a secret. Nevertheless, in principle most of the synthetic minerals used as pigments have been known for a long time.

One of the more recent discoveries in the field of synthetic minerals used as pigments is the molybdenum orange, the formation of which offers some interesting features of general interest.

Schultze (1863) observed that some specimens of wulfenite, $PbMoO_4$, occurring together with crocoite, $PbCrO_4$ were strongly colored. $PbCrO_4$ is monoclinic and $PbMoO_4$ is tetragonal. He suggested as a possible explanation that the deep color of a solid solution of lead chromate and lead molybdate was the result of the stabilization of lead chromate in a tetragonal form which, by itself, does not occur in nature. He proved his point by synthesizing solid solutions of crocoite and wulfenite. Indeed, the molybdate was found to stabilize up to 42 per cent $PbCrO_4$ in the otherwise instable tetragonal modifi-

cation. These crystals are deep orange, i.e., they are much more strongly colored than the pure lead chromate.

More recent work including the atomic structures as determined by X-rays and the establishment of the binary phase diagram confirmed Schultze's explanation. $PbCrO_4$ is trimorphous forming a rhombic, a monoclinic, and a tetragonal form. Depending on the pH of the solution and the coprecipitation of other lead salts, in particular $PbMoO_4$ and $PbSO_4$, pigments having a variety of hues could be obtained.

Synthetic molybdenum orange is one of the newest developments in the field of synthetic mineral pigments. Its interesting history, theory and manufacture including the patent literature can be found in the book "Molybdenum Compounds" (16).

The principle, namely, the synthesis of a desirable modification of a polymorphous mineral by coprecipitation or by proper nucleation, is of great general importance. The optical properties, light absorption, fluorescence, refractive index and dispersion of a compound change with its structure. The modifications of $TiO_2$, rutile, anatase and brookite, have different refractive indices and, consequently, different covering power. For pigment purposes rutile seems to be the most desirable modification of $TiO_2$.

The whiteness of paint or of a porcelain enamel is the result of a multiple reflection of light at the surfaces of tiny crystals which must have an index of refraction either higher or lower than that of the surrounding medium, varnish or glass. The opacity of these systems is a complicated function of the number, size and shape of the particles and of the absolute difference between their refractive index and that of the matrix in which they are embedded.

The manufacture of glasses and enamels takes advantage of the low indices of the minerals villiaumite, NaF ($n = 1.33$) and fluorite, $CaF_2$ ($n = 1.43$) in order to produce opacity (milk glass). Fluorides are added to the batch whose composition is chosen carefully so that these minerals crystallize out on cooling of the melt or on reheating of the glass to its softening range.

A very high degree of opacity is obtained in porcelain enamels by selecting compositions from which minerals precipitate which have a high index of refraction. Cassiterite, $SnO_2$ ($n = 2.0$) has been widely used in the past but has been replaced by baddeleyite, $ZrO_2$ ($n = 2.2$) and by rutile, $TiO_2$ ($n = 2.7$).

The use of rutile as a white pigment and an opacifier has gained considerable importance in the last twenty years and today this synthetic mineral is probably the most widely used opacifier in the field of porcelain enamels. The synthesis of rutile for pigment purposes has grown into a major chemical industry.

A successful scientific approach to the manufacture of white pigments had to wait until X-ray diffraction and, particularly, the electron microscope became available as tools for studying the structure and the particle size of these minerals. The optimum pigment properties call for crystals of a size range from 0.1 to 1.0 micron which is beyond the usefulness of the petrographic microscope.

The scattering power of $TiO_2$ is higher than that of other white pigments. If the tinting strength of rutile in arbitrary units is set equal to 100, that of

ZnS is 50 and that of ZnO only 23 units. $TiO_2$ in the form of anatase has a lower tinting power (75) than rutile. One method of its synthesis involves two steps, precipitation of anatase and its transformation into rutile. Titanium ores are digested with sulfuric acid under reducing conditions. On diluting the liquor the titanium sulfate hydrolyzes whereas iron in the reduced form remains in solution as ferrous sulfate. After several leaching and washing operations the precipitate consists of tiny crystals of anatase which still contain a considerable amount of sulfate ions adsorbed at their surfaces. These crystals, however, are too small to have good pigment qualities so that they have to be subjected to a recrystallization process. Calcination drives out the water and most of the adsorbed sulfuric acid, and at the same time it causes the size of the crystals to increase. Under controlled heat treatment the anatase modification of $TiO_2$ changes into rutile. An excellent discussion of the factors which influence the pigment qualities of this mineral has been presented by W. Hughes (17).

The mineral lazurite or lapis lazuli ranks among the most highly valued minerals since the earliest times. It has been found in the treasure house of Pharaoh Rameses. It was a favorite of the ancient Babylonians and Assyrians who compared it with the deep blue sky of the oriental night and its pyrite inclusions with the sparkling stars. This mineral in spite of being rather widely distributed is not found in great quantities. In the middle ages it was imported into Europe from Afghanistan and from Tibet. Marco Polo (1271) described the tedious process of extracting from it a dark blue pigment called ultramarine which was very much in demand and sold for as high as $30 a pound. Its analysis by Clément and Desormes (1806) revealed its composition to be 35.8 per cent $SiO_2$, 34.8 per cent $Al_2O_3$, 23.2 per cent $Na_2O$, 3.1 per cent S and 3.1 per cent $CaCO_3$. Ever since that time the color and composition of this mineral have been a puzzle to the chemist. Blue minerals and artificial pigments contained either copper, iron or cobalt, but this mineral did not contain any element which normally would be associated with its color.

At the beginning of the 19th century a chance discovery, a blue crust in a soda ash kiln, and its analysis by Klaproth and Vauquelin revealed the possibility that the much coveted pigment could be synthesized. The Société d'Encouragement in Paris (1824) offered a prize of 6,000 francs for a method of manufacturing ultramarine. In the year 1828 Guimet (Toulouse), Gmelin (Tübingen) and Köttig (Meissen) published methods of synthesizing the blue pigment and a few years later ultramarine was manufactured commercially. With few alterations (using soda ash instead of sulfate) this process is still in use and large quantities of ultramarine are being produced by heating together kaolin, quartz, soda ash, sulfur and carbonaceous material. It was found that the blue color could be varied by treatment of the product with different gases and reddish and green hues have been obtained.

From a chemical point of view the ultramarine is one of the most interesting minerals. In its reactivity it resembles the group of zeolites. Its alkali can be replaced by silver. The resulting yellow silver ultramarine, in turn, can be further modified by replacing the silver by other metal atoms.

*2. Phosphors.*—One day in the year 1600 Vincencio Casciarola, an Italian bootmaker, who, in his spare time, engaged himself in alchemical experiments, made an exciting discovery. When looking for the "Philosopher's Stone" he found an exceptionally heavy rock in the neighborhood of his native Bologna which looked to him like a promising source for gold. This mineral, barite $BaSO_4$, after calcination proved to be even more miraculous than the expected gold; it had acquired the power to store sunlight and to emit it in the dark for hours. This "Stone of Bologna" was the first synthetic fluorescent and phosphorescent material, consisting of barium sulfide, activated by heavy metal ions.

The phenomenon of phosphorescence was studied intensely during the second half of the 19th century by Becquerel, Crooks, Stokes and many other scientists. At the beginning of this century, Lennard and his School described the preparation of a large number of mineral substances which had the ability to store light energy and emit it in the dark. Their preparation did not differ greatly from the first phosphor obtained by Casciarola in 1600. Further research revealed that many oxides and sulfides can be "activated" by traces of heavy metals and will then fluoresce on exposure to ultraviolet light. This interesting class of mineral substances, primarily sulfides of the alkaline earth group, often referred to as Lennard-Phosphors, remained a laboratory curiosity until a few years ago.

When the laws governing the radiation of solids as a function of their temperature were derived by the classical physicists, it was found that all artificial light sources from the candle to the incandescent lamp and the electrical arc did not use the available energy economically. In order to produce light most of the chemical energy contained in the fuel or the electric energy supplied to the lamp had to be converted into heat. The economy of light sources could be improved by the use of radiant bodies at higher temperatures but the melting points of available materials limited further improvements in this direction.

Electrical discharges in gases were found to provide a much more efficient way to convert electrical into radiant energy. However, the energy emitted as the result of gas discharges lies primarily in the ultraviolet region and cannot be used as a light source unless it is converted into radiation of longer wavelengths. With the development of "cold light sources" or "fluorescent lamps" the manufacture of phosphors became an important branch of mineral synthesis. The relatively high price of these phosphors as compared with that of the ingredients, ZnO, ZnS, $SiO_2$, etc., attracted many enterprises to attempt the synthesis of fluorescent minerals. However, in order to produce efficient phospors the purity of the materials has to be extremely high so that this branch of mineral synthesis remains a specialty of a few producers.

Today phosphors are produced for a variety of purposes, X-ray screens, fluorescent lamps and television screens. Depending on the purpose, these phosphors represent a large group of diversified compounds, sulfides, selenides, silicates, germanates and halo-phosphates (synthetic minerals belonging to the apatite family). The constituents are mixed intimately and brought to reaction by the application of heat, often in the presence of a catalyst (mineralizer). The principal difficulty in the synthesis of fluorescent minerals is the

removal of those impurities (iron) which in minute concentrations decreases the efficiency of the phosphor.

*3. Crystals for Ultraviolet and Infrared Transmission.*—The examination of emission spectra has developed into an important tool in the analytical laboratory. In the past mineralogists depended strongly on the flame test for identifying minerals and detecting certain constituents such as lithium, strontium, barium or copper. When performing flame tests Reich and Richter (1863) observed some unusual blue and purple lines in the spectrum of a zinc ore from Freiberg. It was this observation which led to the discovery of the element indium. Flame spectroscopy as developed by Bunsen and Kirchoff was limited to the visible region of the spectrum because lenses and prisms made from glass did not transmit light of much longer (infra-red) or shorter (ultra-violet) wavelength.

It has been found that the usefulness of absorption and emission spectra could be greatly increased when the range of the spectrum can be extended into the ultra-violet and infra-red regions. This extension called for a replacement of the glass optic by lenses and prisms which transmit the ultra-violet (quartz) and the infra-red (rocksalt) regions.

Today sodium chloride is grown commercially for this purpose by controlled cooling of its melt. It extends the practical transmission range for spectrographs up to 15 microns. Sylvite (KCl) goes even farther into the infra-red (20 microns). Potassium iodide, KI, a halide which does not occur in nature, transmits up to 30 microns.

## MINERALS WITH DESIRABLE ELECTRICAL PROPERTIES.

The rapidly developing electronic industries are demanding more and more materials with highly specific electrical properties. Mica, for example, has always been the electrical insulator par excellence. Minerals of the mica group belong to the most common rock-forming minerals, but the occurrence of large single crystals is limited to a very few localities (India).

There are two major avenues of approach to the problem of providing mica for the electrical industries and both are being studied thoroughly at the present time. As mica is plentiful in the form of small crystals, one considers the possibility of preparing a mica sheet by integrating a large number of small plates into a partly oriented single unit. Orientation is essential because the electrical properties of mica depend upon the crystallographic direction. This process, no doubt, has a considerable future. The second approach is the complete synthesis of mica, i.e., to start with the oxides and synthesize large crystals from the basic constituents either from the melt or by solid state reaction.

Members of the group of mica minerals have been synthesized in the past by using the hydrothermal method. In this case the water does not only play the role of a "mineralizer" or "catalyst" as in the synthesis of quartz and of willemite, but water participates in the structure of mica in the form of $OH^-$ groups. Based on crystal chemical principles and on the experience of mineralogists that $OH^-$ ions and $F^-$ ions can replace one another in the more complex structures (apatite, topaz), a method was developed by the Siemens-

Schuckert Werke A. G. in Germany (18) to produce mica crystals from the dry melt. These mica crystals (phlogopite) have electrical properties which are similar to those of the natural mica, but as they do not contain $OH^-$ groups they can be grown without the application of high pressures. The constituents, silica, alumina, calcium, magnesium and potassium in the form of fluorides, silico fluorides, and oxides were fused in platinum or graphite crucibles and the melt allowed to crystallize in a temperature gradient.

Among the electrically conducting materials, graphite is an indispensable mineral in the electrical industries. From the carbon filament of the original incandescent lamp to the huge graphite electrodes used by the electrochemical industries and the anodes of power tubes of modern design, a steady development has refined the processes of graphite manufacture. There are numerous properties which make graphite an indispensable and unique material: its low vapor pressure at high temperature combined with its electrical conductivity are the most striking features, but mechanical strength is not less important.

All carbonaceous materials can be transformed into graphite at high temperature in the absence of oxygen, but petroleum coke is the predominant raw material for electrographite. Careful selection and inspection of the raw material is essential in order to keep the ash content of the graphite at a minimum (0.2–0.5 percent). Certain electrolytic processes require a graphite with less than 0.05 percent ash and large quantities of graphite in its purest form were prepared during the last world war in connection with the Manhattan Project.

The process is basically the same as that conceived by E. G. Acheson in 1896. According to the inventor's view that graphite is a secondary material resulting from the thermal dissociation of boron carbide or silicon carbide, the original patent calls for additions of silica and boric oxide. Today these additions are no longer used. Graphitization begins above 2000° C and is accomplished in electrical furnaces of various design and various sizes.

## MINERALS WITH DESIRABLE MAGNETIC PROPERTIES.

Centuries before the beginning of the Christian era it became known that a certain iron ore had the mysterious property of attracting small bits of metallic iron. This iron ore, magnetite, a ferrous ferrite ($FeO \cdot Fe_2O_3$), represents a natural magnet. It took a long time until it was learned that stronger magnets could be obtained by bringing pieces of iron into electrical coils and that an electric current would induce magnetism in the iron. The electrical age with all its conveniences of producing and distributing electrical power, telephone, telegraph, radio and television, became feasible only through this relation between electricity and magnetism. In the course of time it was discovered that iron cores are not ideal magnets when used in connection with high frequencies. Electrical energy is dissipated in these materials and precautions had to be taken to keep the loss through "eddy currents" at a minimum (use of laminated or powdered metal as cores).

Furthermore, metallic iron was found to be inferior to some of its alloys. On the basis of alloys containing Ni, Co, Mo and other metallic elements besides iron, magnets of superior quality could be produced. In all these devel-

opments the natural magnet, the mineral $Fe_3O_4$, was completely ignored because it seemed far inferior to the metals.

With the development of television, however, spinels are being used increasingly for electronic equipment which has to operate in the frequency of 10 to 5,000 kilocycles. In this frequency range certain ferrites were found to be superior to the ferromagnetic metals. This group of synthetic minerals corresponds to the natural spinels, especially those which contain $Fe_2O_3$ and $Cr_2O_3$ in the place of $Al_2O_3$. The systematic exploration of ferromagnetic spinels started only in the last two decades and is primarily connected with the names of N. Kawai in Japan, J. L. Snoek and E. J. W. Verwey in Holland and L. Neel in France.

Permanent magnets can be obtained by allowing some spinels to cool in strong magnetic fields from temperatures above 300° C to room temperature. For this purpose (hard ferro spinels) solid solutions of the ferrites of FeO, NiO and CoO have been found most useful.

For temporary magnets spinels are used which are based on solid solutions of the ferrites of NiO and ZnO. All of these minerals are synthesized by solid state reactions using the same methods as for the spinels which are used as pigments. Wet grinding and ball milling leads to a fine powder. After evaporating the water, the powder is molded by dry pressing in polished steel molds and subsequent sintering. Heating to temperatures up to 1400° C in air completes the synthesis and produces a homogeneous spinel.

The spinel structure tolerates a great number of variations, a fact which makes this mineral a unique material for substitutions in nature and in the laboratory. In the past the spinel group was used primarily for ceramic pigments. Today its magnetic properties are in the foreground and research on synthetic spinels is carried out in several laboratories.

### MINERALS WITH DESIRABLE THERMAL PROPERTIES.

We have seen that one use of graphite by the electrical industries is based primarily on a combination of electrical conductivity and low vapor pressure at extremely high temperature. Graphite is an important refractory material used for crucibles and as a construction material for high temperature furnaces.

A rather rare mineral, cristobalite, a high temperature form of silica, is manufactured on a large scale by heating quartzite with the proper catalyst (lime) and transforming it into its high temperature modifications tridymite and, particularly, cristobalite. All three modifications, quartz, tridymite and cristobalite, have identical chemical compositions, $SiO_2$, but different physical properties. The melting point of cristobalite is about 100° C above that of the quartz. In addition its thermal expansion characteristic in the high temperature range makes cristobalite a desirable mineral for the construction of furnaces.

Another rare mineral, mullite, $3Al_2O_3 \cdot 2SiO_2$, which is closely related to sillimanite, $Al_2O_3 \cdot SiO_2$, is synthesized on a large scale because of its highly refractory properties. These aluminum silicates form in ceramic bodies where they provide both mechanical strength and refractory properties. Mullite is

also obtained by fusion and is a valuable material for tank blocks used in the glass industry. Whereas the mineral mullite is rare in nature, some related minerals, kyanite and andalusite, both having the formula $Al_2O_3 \cdot SiO_2$, occur in sufficient quantity to make them a valuable source for synthetic mullite. At high temperature both aluminum-silicates, kyanite and andalusite, undergo decomposition yielding mullite and a more siliceous matrix.

Corundum, $Al_2O_3$, is a refractory which combines high melting temperature with high temperature strength. Corundum is obtained as single crystals by the flame fusion process, as a polycrystalline aggregate by sintering alumina at temperatures around 1800° C (sinter corundum), and finally as an electrocast product.

Periclase is another rare mineral whose synthesis is performed in large scale operations, because it combines resistivity towards basic slags with extreme refractoriness.

One would think that this list of refractory minerals would provide an ample selection for all practical purposes. Nevertheless, the search for new refractories is going on and will go on with the development of metallurgy. New metals are introduced as construction materials. Metallic titanium, a laboratory curiosity of a few years ago is now beginning to compete with steel in the aircraft industry. Its combination of strength and light weight makes it a promising construction material of the future. However, its manufacture is difficult and calls for special refractories. A large number of high melting oxides, sulfides, and nitrides are being examined for this particular purpose.

Among the refractory materials, natural minerals are nearly completely replaced by synthetic ones: cristobalite, periclase, corundum, etc. In the field of thermal insulators, however, the natural mineral asbestos still maintains its leading position and it is not likely that synthetic asbestos will replace the natural mineral in the near future.

Asbestos has two unique properties, the strong surface forces emanating from the fibrous structure and its resistance to heat, which make it a unique material for brake linings. Its fluffiness makes it an unsurpassed thermal insulator for high temperature, e.g., for steam line packings. Whereas in the low temperature region (refrigerators) glass fibers have replaced asbestos, no substitute for natural asbestos has yet been found for these two important applications: brake linings and high temperature insulation.

One approach which has been considered to ease the present asbestos shortage is the integration of short fibers to long ones, corresponding to the integration of small mica crystals to sheets. Orientation of asbestos fibers in electrical fields and combining them have been attempted but apparently no practical method has been developed.

As far as the synthesis of asbestos is concerned, the problem has not advanced as far as the synthesis of quartz crystals or even that of mica crystals. Several attempts to synthesize asbestos have been reported from mineralogical laboratories in Switzerland (P. Niggli, E. Brandenberger) and in Germany (W. Noll, W. Jander) but only microscopic fibers have been obtained so far. Two methods were used, the hydrothermal synthesis and a precipitation method using soluble sodium silicates and magnesium salts as the components.

There is no evidence that asbestos, which is a hydrosilicate of magnesium, can be replaced by a synthetic mineral which contains $F^-$ ions instead of $OH^-$ ions (phlogopite-mica relation).

Some minerals have thermal expansions which are either very low or even negative in some crystallographic directions, e.g., cordierite, $2MgO_2Al_2O_35SiO_2$, eucryptite, $Li_2OAl_2O_32SiO_2$, and a high temperature form of spodumene, $Li_2OAl_2O_34SiO_2$. These minerals are valuable constituents of special ceramic bodies with low expansion and high resistance to thermal shock.

The group of natural and synthetic lithium minerals offers an interesting theoretical problem because of their unusual expansion characteristics and the occurrence of contraction on heating. The theoretical and practical aspects of the thermal properties of lithium alumino silicates have been studied by F. A. Hummel (19). His research led to the development of a new ceramic body "Stupalith" which contracts slightly on heating.

### SYNTHESIS VERSUS SUBSTITUTES.

Iceland spar, on account of the large size of single crystals, their transparency and birefringence, became an indispensable material for petrographic microscopes and other optical instruments utilizing polarized light. Since the supply of this mineral is limited, the problem arises as to whether or not it may become necessary to synthesize large single crystals of calcium carbonate for Nicol prisms. It has been found, however, that another mineral, the Chile saltpeter, $NaNO_3$, which is homomorphous with calcite has similar optical properties and can be used as a substitute for Iceland spar. Chile saltpeter does not occur in large crystals in nature, but large crystals can be grown easily from the melt. Today $NaNO_3$ crystals weighing several pounds are produced for Nicol prisms; their optical quality is equivalent to that of selected crystals of Iceland spar. C. D. West (20) found that mica plates act as insoluble and unmeltable seeds for sodium nitrate. In contact with the melt the $K^+$ ions of the mica surface are replaced by $Na^+$ ions. The latter form a hexagonal net of $Na^+$ ions whose side is 5.17A. The modified cleavage plane of mica thus constitutes, so to speak, the first crystal plane of the sodium nitrate which grows from the mica into the melt as a single crystal. This is a typical example for those cases where a substitute mineral ($NaNO_3$) can take the place of one which was used originally ($CaCO_3$), as long as large crystals are available.

A similar situation arises for mica where the synthesis of the muscovite requires high pressures and would be extremely difficult and costly. By a suitable change of composition the mineral phlogopite is formed which can be synthesized under normal processes. As a substitute for mica, minerals of the clay group have been used. These minerals have a similar atomic structure but form extremely small plates which have to be lined up in order to take advantage of their directional electrical insulating properties. E. A. Hauser (21) developed a promising process which led to a substitute for mica (Alsifilm).

Twenty of the 32 crystal classes have no center of symmetry. If a shear stress is applied to a crystal without a center of symmetry, the shift of the electrical charges of the ions produces an electrical effect (piezoelectricity) which can be used to change acoustical waves into electrical impulses. Among the crystals which meet these requirements the most important ones are tourmaline, quartz (natural and hydrothermal), rochelle salt, ammonium dihydrogen phosphate and lithium sulfate monohydrate. With the exception of quartz these crystals can be grown from aqueous solutions and are produced commercially. Which one of these crystals is the best suited depends on the frequency range and on the temperature conditions. Its very low temperature coefficient of the piezoelectric response makes quartz a most valuable mineral for oscillator control. The search for new piezoelectric materials is still going on. S. Zerfoss and associates (22) investigated the crystal chemical relations in piezoelectric materials as a basis for a search for substitutes.

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# ACETONIC DITHIZONE IN GEOCHEMISTRY.

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ABSTRACT.

In a previous paper we described a dithizone-emulsion technique by which it was feasible to detect as little as 0.001 p.p.m. (parts per million) of copper and zinc in natural waters.

In practice this method has one major drawback. The dithizone has to be introduced in the form of an ammoniacal aqueous solution which is not stable and normally must be renewed once or twice each day.

An acetonic solution of dithizone is much more stable than an aqueous one. This stability makes it possible in the field to use an acetonic solution of dithizone for weeks, or even months if temperatures remain below 80° to 90° F.

The use of acetonic dithizone affords new possibilities in field and laboratory techniques which are discussed.

## INTRODUCTION.

In recent years we have improved the techniques for discovering the presence of heavy metals in natural waters. These improvements were necessary if these techniques were to be practised in those areas where extreme dilutions are apt to be caused by heavy run off from rain, melting snow, and ice fields.

Our techniques involved adding to natural water dithizone as a solution in aqueous ammonia, and collecting the resulting metal dithizonates and excess reagent by means of an emulsion of xylene which would break up under acid conditions and gather at the upper surface of the liquid. However, the relatively rapid oxidation of ammoniacal dithizone solutions has proved troublesome to prospectors. Fortunately we developed (2) a method for copper determinations by which copper and dithizone reacted in a homogeneous acetonic solution. Arising from this development we found that an acetonic solution of dithizone also provided a convenient way of adding small amounts of dithizone to water. Furthermore, this acetonic solution of dithizone keeps even better than a stock solution of dithizone in carbon tetrachloride, from which we had previously prepared our ammoniacal dithizone solutions as they were needed.

If there is sufficient metal in water that is being tested the metal dithizonate that is formed becomes visible to the eye and need not be collected by means of an emulsion. Furthermore, it is possible to destroy any excess dithizone with dilute nitrite which will not, however, attack the metal dithizonate: thus any purple color remaining after nitrite has been added must be caused by a metal complex.

REAGENTS.

*Dithizone Solution.*—Dissolve sixty milligrams of dithizone per litre in chemically pure acetone, which need not be anhydrous. The resulting solution should be emerald green. A trace of a metallic salt, even of a light metal, can turn this solution deep orange. As far as we have been able to ascertain this orange color is caused by a molecule to molecule combination of dithizone with the metal salt, similar to those of the fatty acids with their salts. An orange colored solution can be used for a short time after it is formed. In practice this is for as long as the green color can be regenerated by adding a strong acid, in which case the reagent combines as previously with heavy metals. Both the orange solution and the regenerated green solutions oxidize rapidly—in a matter of hours. The factors governing this oxidation are not understood but even with moderate temperatures these solutions cannot be expected to last more than a day.

Accidental contamination in the field by other reagents, particularly acetate, may necessitate frequent renewal of the acetonic dithizone solution.

Instead of dissolving solid dithizone in acetone it may be more convenient when preparing small volumes to dilute a chloroform solution of dithizone. If, for example, 1,200 milligrams of dithizone are dissolved in one litre of chloroform, then one volume of this solution may be added to 19 volumes of acetone and the resulting homogeneous liquid will behave as would a simple acetonic dithizone solution. Chloroform is soluble enough in water to disappear, when it is added to water. This is in contrast to carbon tetrachloride which is insoluble in water and where present in acetone will separate into small droplets retaining all or most of the dithizone in a form which could not react readily by simple diffusion with metals present in water.

*Xylene Emulsion.*—Make a 1 percent solution—or pseudo-solution—of sodium laurylsulfonate, or Duponol C, carefully checked to be sure that it is free from heavy metals, in distilled water. Then add to 10 ml of the above solution in a 250 ml pyrex bottle 5 ml of chemically pure xylene. Xylene may be considered satisfactory if a deep emerald green solution of dithizone in it does not become yellowish green in a few days time, if the mixture is kept cool and in the dark.

Shake the xylene and laurylsulfonate—or Duponol C—until emulsified. Then add 10 ml more of xylene and shake again until the whole is emulsified. Continue adding xylene, shaking each time until emulsification is complete, until 90 ml of xylene have been added; never add a greater volume of xylene at any one time than the volume of the liquid already in the bottle. Incidentally, if no shaking machines are available and hand shaking must be employed, we recommend a 500 rather than a 250 ml pyrex bottle. After all the xylene has been added, shake a further 5 or 10 minutes, or at least until the creamy emulsion does not separate on standing. This emulsion should then be tested. To do this add 1 ml of emulsion to 100 ml of slightly acid water and stir. After thorough mixing, the liquid should remain milky for from 15 to 20 seconds. If the solution takes longer than half a minute to clear, it may be just as efficient, or even more so, but it is less practical for field use.

The attaining of just the right consistency in the emulsions still remains an empirical matter, probably best coped with by frequent sampling during the ultimate phase of shaking.

*Hydrochloric Acid.*—Add 1 volume of concentrated acid to three volumes of pure distilled water making an approximately 3 N solution. Chemically pure acid is usually satisfactory as it is: the residue obtained from evaporating 10 ml to near dryness should contain less than 10$\gamma$ of heavy metals expressed as zinc, by means of the test described below.

If commercial hydrochloric acid has to be distilled use an all glass apparatus and first dilute the acid with its own volume of distilled water.

*Acetate Buffer.*—Dissolve 250 grams of sodium acetate and 10 ml of acetic acid in one litre of distilled water. Purify by shaking with successive portions of a carbon tetrachloride solution of dithizone until the dithizone no longer turns pink but remains partly uncombined giving a dark purple, grey, or green colour to the liquid.

*Standards.*—One hundred milligrams per litre solutions of copper and of zinc of normal acidity will keep indefinitely in pyrex glass. However, before using they should be diluted 25 times making a solution with only 4$\gamma$ per ml. This diluted standard will keep for a day.

*M:5 Sodium Nitrite.*—Dissolve 13.8 grams per litre of chemically pure sodium nitrite in distilled water: if necessary this solution can be purified similarly to the acetate buffer, that is by shaking with dithizone in carbon tetrachloride solution which does not react appreciably with this neutral salt. However, an appropriate amount of this nitrite in an acid solution destroys free dithizone in suspension without affecting measurably the metal dithizonate complex when both remain precipitated in water.

## SPECIAL WARNING.

In a hydrogeochemical work no rubber should be used because it contains metals introduced either as catalysts for vulcanization or as filler. Glass stoppered bottles should be used, preferably pyrex or similar material, wherever practicable. Cork stoppers are usually acceptable in lieu of glass, except for hydrochloric acid which should then be more diluted.

All glassware should be cleaned scrupulously with strong hydrochloric before initial use and thereafter as circumstances indicate. A good way of removing traces of metals from beakers is to make a preliminary zinc determination on metal-poor water. The dithizone solution effectively removes any metal clinging to the glassware.

## PROCEDURE.

### *Testing Water That Contains Less Than 20 $\gamma$ Per Litre.*

This is the usual case, unless there is mineralization in the vicinity. Except that dithizone is introduced as an acetonic rather than ammoniacal solution, the principle and method are fundamentally the same as has already been described (1, 4).[1] Briefly the procedure becomes as follows:

[1] Numbers in parentheses refer to Bibliography at end of paper.

*Copper Only.*—To 100 ml of water add 0.25 ml of hydrochloric reagent or enough to bring the pH to approximately 3. Then add from a few drops to 1 ml of acetonic dithizone depending on the amount of copper present, which is roughly known either from a preliminary test or from inference. Then introduce 1 ml of xylene emulsion and stir vigorously observing the color after about one minute. Great variations, both diurnal and seasonal may occur in some areas and thus attempts at precision are largely illusory. Consequently, we recommend that it is usually sufficient to note the colors obtained from various prepared standards and make a color chart by which the color obtained from any test may be interpreted approximately in terms of metal contents. If precision is needed it can best be obtained by making successive tests until a grey mixed color results from adding a specific amount of dithizone.

*Zinc Only.*—In practice we have not found it convenient at these dilutions to mask the copper by combining it in a colorless complex, such as thiosulphate or dithiocarbamate, or to remove any copper dithizonate before testing for zinc. It is simpler and safer to estimate both metals and deduct the dithizone used for copper.

*Copper plus Zinc.*—Proceed as for copper only except that hydrochloric is replaced by acetate buffer to bring the pH to approximately 5.5. To produce the same mixed colors smaller amounts of zinc are needed than is the case with copper.

### *Testing Water That Contains More Than 20γ Per Litre.*

When prospecting in a well mineralized area it may be necessary to make a great number of tests in a comparatively short time. However, the metal content of natural water in such an area generally is comparatively high. In good light, the color obtained with water containing around 20γ of metal per litre may be directly detected by eye in a 100 ml beaker or in a 3-inch test tube.

Mixed colors cannot be used because dithizone in water either turns purple, when very acid, or orange with acetate buffer. In order to use a mixed color method it is necessary to collect the colored products by shaking them with a little carbon tetrachloride or some other organic solvent. However, we have found it simpler to destroy the excess of dithizone with nitrite which turns dithizone to a very pale yellow color. The actual amount of nitrite to be added depends on temperature and pH of solutions involved and can best be determined empirically in the field. At pH 3 dithizone is destroyed immediately by one part in one thousand of the nitrite solution at 20° C and in 30 seconds at 0° C. The copper complex does not suffer appreciably in 10 or even 100 times longer. Other factors remaining equal, amounts needed at pH 5.5 used for zinc are at least 10 times those used for copper at pH 3.

*Detection of Copper.*—Add hydrochloric solution as if about to use emulsion, and then dithizone until the pink color turns purplish. Then add a suitable amount of nitrite, as described above. If the color fades greatly, too much dithizone has been added and another test should be made trying to obtain a color slightly redder than that remaining after adding the nitrite in the previous test. Then add nitrite as previously.

*Detection of Copper and Zinc.*—Add acetate buffer, and then dithizone. In the absence of metal the dithizone would turn orange because of the acetate in the buffer. Similarly any excess dithizone, above that needed for the metal present, would turn the pink color to orange. Thus, dithizone should be added until the pink of the metal dithizone becomes orange. Then destroy excess dithizone by adding a suitable amount of nitrite. If the color fades very much, make another test as described above for copper.

*Quantitative Estimations.*—Compare colors obtained by using the above methods in conjunction with standards obtained from pure water to which varying amounts of metal have been added.

Very large amounts of ferric ions—above 500γ per liter, destroy some dithizone and may cause an error.

Some other metal ions, such as lead, can behave like zinc in the above tests. However, they appear rarely in natural water unless this water traverses rich mineralization. Manganese and iron do not react.

These methods can be used to ascertain that heavy metals, in the form of ions at least, are below harmful standards in water.

## GENERAL OBSERVATIONS.

Although reproducible results have been obtained by various workers we must warn untrained persons that, in spite of its apparent ease, this method is liable occasionally to give much too high results because of unexpected contamination. Copper and zinc are so widespread in everyday tools and equipment that they can easily be introduced accidentally into an assay. High results should always be checked by duplication.

## ACKNOWLEDGMENTS.

This paper is based on laboratory work which was carried out in the biogeochemical laboratory of the Department of Geology and Geography of the University of British Columbia. The income which has maintained this laboratory has come both from the Department and in varying amounts from various sources to all of whom we acknowledge our indebtedness: The National Research Council, The Defense Research Board, The Consolidated Mining and Smelting Co., Ltd., and the President's Committee on Research have all made contributions during the period when this particular research either was in progress or was being tried out in the field.

The acetonic emulsion technique has been tried out in the field at various localities but most thoroughly by prospecting parties employed by Kennco Explorations (Canada) Ltd. Geochemistry in general and the authors in particular owe much to the willingness of this company to pioneer in this new field.

UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, B. C., CANADA,
*Feb. 11, 1953.*

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1. Delavault, R. E., and Irish, R. I., Emploi de la dithizone en solution aqueuse ammoniacale: Séances Acad. Sci., Comptes Rendus, vol. 229, p. 1079–1081, 1949.
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4. Warren, H. V., Delevault, R. E., and Irish, R. I., Improved dithizone field test for heavy metals in water: Geol. Soc. Amer. Bull. 62, p. 609–618, 1951.
5. Webb, J. S., and Millman, A. P., Heavy metals in natural waters as a guide to ore: a preliminary investigation in West Africa: Inst. Min. and Metallurgy, Bull. 518, p. 2–16, 1950.

# DISCUSSION

## *BANDED IRON FORMATIONS*

*Sir:* A characteristic feature of many of the highly siliceous, Precambrian, "banded iron formations" is extraordinarily intricate folding. The folds are mostly of small dimensions and they are, in many places, fractured and faulted. This elaborate crumpling of such hard, brittle rocks as those composing the iron formations has been a puzzle. It has been customary to assume that it must have occurred in Van Hise's "zone of flow" where the rocks were deeply buried, with fracturing following at a later time when they were nearer the surface. This explanation did not, however, satisfactorily account for the conditions met with in many localities. The writer was gradually led to the conclusion that the complex folding occurred before colloidal silica was completely crystallized, that is, while it was still in a plastic state. This idea was expressed in the following terms several years ago: "I have come to the conclusion that the silica and iron were laid down in the colloidal state and that before they were crystallized to a hard, brittle state they folded very readily. Later, after becoming cryptocrystalline and brittle, they fractured more readily than they folded." [1] It is believed that this was the first time such a suggestion was offered to explain the phenomena and it is interesting to find it adopted without hesitation, although no reference is made to the above quotation, by authors of two recent papers.[2, 3] They wrote on banded iron formations as far apart as India and Southern Rhodesia.

The paper by Spencer and Percival is of further interest because they appear to have satisfactorily rejected Dunn's replacement hypothesis for the origin of the banded formations of Singhbhum, India in favor of sedimentary deposition of the silica and at least part of the iron. The hypothesis of replacement by hydrothermal action is not, as far as the writer is aware, held by any Canadian geologist familiar wtih these formations except T. L. Tanton. The evidence from numerous iron ranges strongly opposes the replacement hypothesis for the silica, and favors primary deposition as a chemical sediment. Evidence of cross-cutting relations between the silica and adjacent rocks, something to be expected in replacement formations, is strangely lacking.

E. S. MOORE.

TORONTO, ONTARIO,
*Feb. 9, 1953.*

[1] Moore, E. S., Origin of iron deposits of the "Lake Superior Type": Trans. New York Academy of Sciences, Series II, Vol. 9, No. 2, p. 46, 1946.

[2] Spencer, E., and Percival, F. G., The structure and origin of the banded hematite jaspers of Singhbhum, India: ECON. GEOL., Vol. 47, p. 365, 1952.

[3] Bond, Geoffrey, The deformation of banded ironstones in southern Rhodesia: ECON. GEOL., Vol. 47, p. 823, 1952.

# REVIEWS

**Life and Letters of R. A. F. Penrose, Jr.** By Helen R. Fairbanks and Charles P. Berkey. Pp. 765; pls. 16. The Geological Society of America, New York, 1952.

Since Mr. Penrose became the great benefactor of the Geological Society of America, and to a much lesser extent of the *Journal of Economic Geology*, and the Society of Economic Geologists, his biography becomes of interest to all geologists. The authors of this volume have performed an excellent service in assembling, collating, and interpreting his papers and letters. It is so unusual to find a geologist, who is also an industrialist, and particularly who left a considerable part of his fortune to geological organizations, that Mr. Penrose stands apart from all other geologists. His service to geology in America and to the world is, therefore, unique. His biography is thus particularly welcome.

One recalls with interest his background, his early education, and then his adventures into geology in Texas, with the Arkansas Geological Survey, in Cripple Creek, in Arizona, and in Eurasia. Later his travels took him to Alaska, the Antipodes, and the African Gold Fields—a broadening experience for any geologist. All of these experiences form an illuminating background of the man who became the great benefactor of geology.

In Chapter 11, on "Beginnings of Utah Copper," it is perhaps a bit unfortunate that the authors did not have access to information other than the letters in Mr. Penrose's files, since the abbreviated account omits the earlier phases that led Mr. D. C. Jackling and Penrose-MacNeill into the scene. These were also the initial phases during which Mr. G. C. Gemmel, engineer for Mr. DeLamar, twice examined the property and took options for Mr. DeLamar on the present Utah Copper. During the second option, Mr. Jackling, a chemist at Mercur, was brought up to Bingham Canyon to run a pilot stamp mill to test the dependability of Mr. Gemmel's samples and to determine if the ore could be concentrated. Mr. Jackling determined that it could be concentrated. Mr. Gemmel had come from the Iron Country where steam shovels were used and thought they could be applied to low-grade copper ore also, but Mr. DeLamar, rather fearful of such a new venture, dropped his option. Thereupon, Mr. Jackling took it to Penrose-McNeill, who assisted by Mr. R. A. F. Penrose initiated the new venture with Mr. Jackling as President and Mr. Gemmel as General Manager. Thus, was initiated the great Utah Copper Mine and the wealth of Mr. Penrose, and the great benefaction to geology.

The last 5 chapters deal with Mr. Penrose's relations with the Society of Economic Geologists, the Geological Society of America, and the American Philosophical Society. Here are depicted his broad scientific interests and his increasing concern in the Geological societies. His early interest was the Society of Economic Geologists, of which he was the first President. The reviewer recalls many hours working with Mr. Penrose over the charter of the Society, and in the design of the first Penrose Gold Medal, for the Society of Economic Geologists. Later, with in-

creased attention to the Geological Society of America, he also established the Penrose Gold Medal of the Geological Society of America.

The authors are to be complimented on a fine biography of a man whose foresight led to the establishment of a great fund for progress and research in geology, unheard of and undreamed of prior to the bequest. An excellent Twenty-year Summary of the results of the bequest is given by H. R. Aldrich, the present Secretary of the Society, as a conclusion. We are all indebted to the Geological Society of America for bringing out such a fine volume.

ALAN M. BATEMAN.

YALE UNIVERSITY,
NEW HAVEN, CONN.,
*March 15, 1953.*

**Geology of the Uravan Mineral Belt.** BY R. P. FISCHER AND L. S. HILPERT. Pp. 13; pls. 3; figs. 5. U. S. Geological Survey Bull. 988-A, Washington, 1953. Price, 35 cts.

**Geologic Guides to Prospecting for Carnotite Deposits on Colorado Plateau.** BY DORIS BLACKMAN WEIR. Pp. 27; figs. 8. U. S. Geological Survey Bull. 988-B, Washington, 1953. Price, 15 cts.

Two short publications by the Geological Survey on the geology of uranium show the wisdom of applying scientific methods in the search for uranium ores instead of using hit-or-miss prospecting, Secretary of the Interior Douglas McKay stated today.

If reasonable success is to be obtained in exploring large areas of untested ground with a minimum amount of expensive, time-consuming drilling, geologic guides to ore should be recognized and followed, the Secretary said.

These features and their application to exploration drilling are briefly described in Geological Survey Bulletin 988-A by R. P. Fischer and L. S. Hilpert, "Geology of the Uravan Mineral Belt," and Geological Survey Bulletin 988-B by Doris Blackman Weir, "Geologic Guides to Prospecting for Carnotite Deposits on Colorado Plateau." They represent work accomplished on behalf of the U. S. Atomic Energy Commission and are published with permission of the Commission.

Fischer and Hilpert apply the name "Uravan Mineral Belt" to a narrow, elongate region in southwestern Colorado in which the carnotite deposits (uranium ore) have a closer spacing, larger size, and higher grade than those in adjoining areas. The belt extends from Cateway through Uravan to Slick Rock. Here the Geological Survey has done intensive diamond-drill exploration since 1947, aided by geologic relations of the mineral belt and certain geologic features recognizable in the drill cores.

It has been found that the ore deposits within the belt tend to be clustered in patches of favorable ground 1,000 feet or more in width and usually a mile or more in length. The ore bodies are irregular tabular layers averaging two to four feet in thickness, impregnating sandstone of the Morrison formation. They lie generally parallel to the sandstone formation and range in size from a few feet wide, containing only a few tons of ore to several hundred feet wide, containing many thousands of tons.

The deposits are thought to have formed from ground-water solutions migrating through ore-bearing beds, probably soon after the accumulation of the sands. Precipitation is believed to have resulted from slight changes in the chemical composition of the solutions, perhaps in the environment of decaying organic material.

Fossil tree trunks and branches are common in the ore-bearing sandstone. Some are a foot or more in diameter and as much as 100 feet long. These logs were rafted into place by streams that deposited the enclosing sands.

Also in the ore are peculiar concretionary structures—ore rolls—ranging from 10 to 100 feet or more in length. They lie parallel to the dominant orientation of the fossil logs, having the same general direction of elongation shown by the ore bodies.

"It must be assumed," the authors state, "that some geologic conditions having widespread influence controlled the orientation of the fossil logs and the ore rolls in the area of the mineral belt."

An index map accompanies the text of both publications showing the deposits in the main carnotite-producing region of southwestern Colorado and southeastern Utah. These yielded about 725,000 tons of carnotite ore during the 1936–43 period of intensive mining. Of this amount, 78 percent was mined from deposits in the Uravan belt. A study of the assay data available shows that most deposits in the belt have ratios of about one part uranium oxide to 5 or 10 parts of vanadium oxide.

Maps showing the location of exploration areas, principal deposits, and mine developments indicate many good prospects for future ore production.

Outlining the geologic guides to prospecting for carnotite Mrs. Weir concludes in Bulletin 988-B:

Most ore deposits are in or near the thicker, central parts of sandstone lenses, and in general the thickness of the sandstone decreases away from ore deposits. Sandstone that is less than 40 feet thick is generally not favorable for large ore bodies.

Sandstone in the vicinity of ore deposits is light brown in color. An increasing proportion of sandstone with a reddish color, away from ore deposits, indicates unfavorable ground.

Near ore deposits the mudstone in the ore-bearing sandstone and immediately below it has been altered from red to gray.

Sandstone in the immediate vicinity of ore deposits contains more carbonized plant fossils than do the same beds away from ore deposits.

Exploration that uses these features as guides, according to the author, "yields results that are about twice as good as exploration using little or no geologic guidance."

The Survey exploratory work is done in three stages. First, holes are drilled at a wide spacing, usually about 1,000 feet apart, for geologic information. Next, favorable ground is drilled with holes at a moderate spacing, usually 100 to 300 feet apart, to find ore deposits. In the third stage, holes are drilled about 50 to 100 feet apart to extend and outline any deposits discovered in the earlier drilling.

The geologic features that serve as guides are particularly useful during the first and second stages, for these features have been found to provide larger targets for drilling than do the ore deposits themselves.

**Geologia e depositi de antimonio e di altri metalli del Gruppo dei Monti Romani.** By Gabor Dessau. Centro di Studi per la Geologia dell'Appennino del Consiglio Nazionale delle Ricerche, Pub. 11, Pisa, 1952. Pp. 64 with map, 1:25,000.

Under the auspices of the Center of Studies on the Geology of the Appennines, the author spent four months investigating the geology and mineralization of a region 80 kilometers square in southwest Tuscany. This region, referred to as the Monti Romani, was practically unknown from a geological standpoint. The few investigations that had been devoted to it were largely general and superficial. The

present work is given over to a highly detailed description of the mineral deposits, chiefly antimony, and to the correlation between mineralization and general geological features of the area. The stratigraphic series includes Permo-carboniferous phyllite (Verrucano) overlain by Triassic Cavernous limestone which is in turn thought to be disconformably overlain by the transgressive Tertiary "Macigno" sandstone.

The tectonic pattern is given by a set of tilted blocks dipping northeast and limited by steep fault-planes striking northwest-southeast which are very young, probably of post-Pliocene age. The epithermal antimony deposits consist almost exclusively of great masses of micro-crystalline and concretionary quartz, containing nests of stibnite. These masses are localized where the ore-bearing solutions rising along the fault-planes have been dammed up by the almost impervious Tertiary sediments overlying the Cavernous limestone. The contact between Cavernous limestone and the Tertiary formations can be sedimentary or due to faulting. The author believes in the Quaternary age of both the antimony mineralizations and of the other less important pyrite-barite and Pb-Zn-Cu mineralizations.

The principal result of the author's investigation is a splendid geologic map accompanying the paper, on a scale of 1:25,000.

B. A. BROMBERT.

NEW HAVEN, CONN.,
*April 1, 1953.*

**Waves and Tides.** BY R. C. H. RUSSELL AND D. H. MACMILLAN. Pp. 348; pls. 17; figs. 100. Philosophical Library, New York, 1953. Price, $6.00.

This is a book of interest to the layman, the yachtsman, and the professional. It is written in language for everyone's reading, but at the same time it is written with the authority of two men well qualified by scientific background and experience to deal with each of the subjects.

Following a foreword by Dr. Herbert Chatley is Part I, Waves, by Mr. Russell. He treats of the characteristic of ocean waves, ideal waves, the generation of waves by wind, near-shore waves, wave-induced currents, movement of materials, effect of wave action on structures and wave measuring. An appendix, which can be skipped by the layman, deals with mathematical features, such as velocity, formulae of waves, and energy. References follow each chapter.

Part II, by Commander Macmillan, opens with a discussion of the pulse of the earth, followed by the general features of the equilibrium theory. After this the reader is led into tidal theory and the relation between tides and weather, navigation, energy, research and factors in history, commerce and sea-power. Brief appendices follow on the determination of mean sea level and formulae.

Both parts are illustrated by many photographs and line drawings. For anyone interested in these two phases of oceanography, this is a book to turn to.

**Economics of Natural Gas in Texas.** BY J. R. STOCKTON, R. C. HENSHAW, JR., AND R. W. GRAVES. Pp. 316; pls. 38; figs. 19; tbls. 87. University of Texas, Austin, 1952. Price, $5.00.

Here is brought together in one volume much scattered information about natural gas in the nation, and in Texas in particular. It is a comprehensive, factual treatment of the economic problems facing the natural gas industry, but also delves a bit into oil, coal, water power and atomic energy. The main subjects covered are history, utilization, employment, production, reserves, transportation, taxation, public

control, conservation and competition of natural gas. The text is accompanied by 87 tables, 38 charts and 19 figures. Two appendices treat of the Railroad Commission and production and value of gas in Texas by counties.

**Structural and Field Geology.** By James Geikie, Robert Campbell, and Robert M. Craig. Pp. 397; pls. 69; figs. 147. Oliver and Boyd, London, 1953. Price, 37/6.

In the 5th edition of this well known textbook, which appeared in 1940, many changes were made particularly in Chapters I–V and XV, and many new illustrations were introduced. In this 6th edition, the revisors state "only minor changes have been made" and the cover jacket reads, "for the present issue it has not been thought necessary or desirable to make many modifications, but opportunity has been taken to make a number of minor changes in the text and to introduce several new photographic illustrations." Five plates have been changed, and the other changes have been so slight that apparently the same type plates were or could have been used for printing. Naturally, none of the newer advances of thought or knowledge that have come forth in the last 14 years, since the previous edition was prepared, have been included. The previous edition was out-moded in many respects; the present one is more so. One finds many out-of-date usages and the references for the most part are now quite ancient. Only a few later than 1940 have been added, and these appear to be about the only changes in the revision, except for the new photographs. It might have been more accurate to call this a reprinting, instead of a revision. In this respect the book is similar to other books that have appeared recently from British publishers without revision, presumably to build up sales for foreign exchange at the minimum of expense of preparation. Such a well known book as this one, if it is worth reprinting, surely would be worth a real revision.

**X-Ray Identification and Crystal Structures of Clay Minerals.** Edited by G. W. Brindley. Pp. 345; illust. The Mineralogical Society, London, 1951. Price, 36 s.

The 14 chapters of this book are written by 11 different authors, each an authority on his subject. The chapters include: I, "Experimental Methods" by G. W. Brindley; II, "The Kaolin Minerals" by G. W. Brindley; III, "Phase Changes which Occur on Heating Kaolin Clays" by H. M. Richardson; IV, "The Montmorillonite Minerals (Montmorillonoids)" by D. M. C. MacEwan; V, "The Mica Clay Minerals": Part I by R. E. Grim and W. F. Bradley, Part II by G. Brown; VI, "The Chlorite Minerals" by G. W. Brindley and K. Robinson; VII, "Vermiculites and Some Related Mixed-layer Minerals" by G. F. Walker; VIII, "Sepiolite" by Mlle. S. Caillère; IX, "Palygorskite-Attapulgite" by Mlle. S. Caillère and S. Hénin; X, "Oxides and Hydroxides of Aluminum and Iron" by H. P. Rooksby; XI, "X-Ray Diffraction by Structures with Random Interstratification" by G. Brown and D. M. C. MacEwan; XII, "X-Ray Diffraction by Randomly Displaced Layer Lattice Minerals" by G. W. Brindley; XIII, "Non-Clay Minerals in Clays" by D. M. C. MacEwan; XIV, "The Interpretation of the Composite X-Ray Powder Diagram" by G. W. Brindley and D. M. C. MacEwan.

The various chapters have been carefully blended together by the editor so that the reader would hardly be aware that they are not by a single author.

The book brings together much formerly scattered information, and considerably new material is added. It is, of course, a book every mineralogist will wish to have.

## BOOKS RECEIVED.

FRANK G. LESURE.

**U. S. Geological Survey—Washington, D. C., 1952–53.**

**Prof. Paper 243-A. Ostracodes from the Upper Part of the Sundance Formation of South Dakota, Wyoming and Southern Montana.** FREDERICK M. SWAIN AND JAMES A. PETERSON. Pp. 15; pls. 2; fig. 1. Price, 36 cents.

**Prof. Paper 248-A and 248-B. Mica Deposits of the Southeastern Piedmont. Part I, General Features.** RICHARD H. JAHNS, WALLACE R. GRIFFITS, AND E. WM. HEINRICH. **Part II, Amelia District, Virginia.** RICHARD W. LEMKE, RICHARD H. JAHNS, AND WALLACE R. GRIFFITS. Pp. 138; pls. 6; figs. 58; tbls. 2. Price, Pt. I—$1.25; Pt. II—60 cents. *Distribution and structure of pegmatite bodies in area, their mineralogical characteristics, and economic possibilities of mica and other minerals.*

**Prof. Paper 252. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications.** LUNA B. LEOPOLD AND THOMAS MADDOCK, JR. Pp. 57; figs. 32. Price, 35 cents. *Quantitative measurement of some of the hydraulic factors that help to determine the shape of natural stream channels: depth, width, velocity, and suspended load, and how they vary with discharge as simple power functions.*

**Bull. 988-C. Uranium in the East Walker River Area, Lyon County, Nevada.** M. H. STAATZ AND H. L. BAUER, JR. Pp. 24–43; pls. 4; figs. 2. Price, 35 cents.

**Bull. 988-D. Distribution of Uranium in Rich Phosphate Beds of the Phosphoria Formation.** M. E. THOMPSON. Pp. 45–67; figs. 12; tbls. 8. Price, 15 cents. *Preliminary studies indicate concentration of uranium in phosphate rock, not wholly due to phosphate content, but may depend partly on organic matter.*

**Water-Supply Paper 1133. Quality of Surface Waters of the United States, 1948.** Pp. 373. Price, $1.00.

**Water-Supply Paper 1138. Geology and Ground-Water Resources of Comal County, Texas.** WILLIAM O. GEORGE, SETH D. BREEDING, AND WARREN W. HASTINGS. Pp. 129; pls. 6; figs. 7; tbls. 21.

**Circ. 225. Geochemical Association of Niobium (Columbium) and Titanium and Its Geological and Economic Significance.** MICHAEL FLEISCHER, K. J. MURATA, JANET D. FLETCHER, AND PERRY F. NARTEN. Pp. 13; tbls. 8.

**Circ. 245. Geology and Pegmatites of Part of the Fourmile Area, Custer County, South Dakota.** ANDREW J. LANG, JR., AND JACK A. REDDEN. Pp. 20; pl. 1; figs. 2; tbls. 2.

**Circ. 248. Preliminary Summary of Reconnaissance for Uranium and Thorium in Alaska, 1952.** HELMUTH WEDOW, JR., AND OTHERS. Pp. 15; pl. 1; tbls. 6.

**Circ. 251. Results of Reconnaissance for Uraniferous Coal, Lignite, and Carbonaceous Shale in Western Montana.** WILLIAM J. HAIL, JR., AND JAMES R. GILL. Pp. 9; pl. 1; tbls. 16. *Only 2 out of 23 areas of carbonaceous material indicated traces of uranium.*

**Base Map of Missouri, edition 1952.** Scale 1:500,000. *Indicates highways corrected to 1952. Topography shown by contours of 200 foot interval. Can be obtained with or without shaded relief.*

**Selected Petrogenic Relationships of Plagioclase.** R. C. EMMONS, EDITOR. Pp. 142; pls. 16; figs. 38; tbls. 11. Geological Society of America, Mem. 52. Price, $2.00. *Detailed study of feldspars from average plutonic and volcanic rocks, rather than pegmatites. Conclude potassic content of plagioclase lower than reported, refractive indices of plagioclase give most reliable information on chemical composition; authors discuss perthites, migration of sodic and mafic ingredients; conclude that a large proportion of granites may be of metamorphic origin. Contains many excellent photomicrographs of feldspars.*

**California Division of Mines—San Francisco, 1952–53.**

**Geologic Log for Ventura Basin Field Trip.** Pp. 7; figs. 7. *Field trip road log.*

**Special Rept. 28. Geology of the Mammoth Mine, Shasta County, California.** A. R. KINKEL, JR., AND WAYNE E. HALL. Pp. 15; pls. 9; figs. 5. Price, 75 cents.

**Wavefront Charts and Raypath Plotters.** ALBERT W. MUSGRAVE. Pp. 60; pls. 5; figs. 28; tbls. 3. Colorado School of Mines Quart., Vol. 47, No. 4, Golden, 1952. Price, $1.00. *Mathematical developments leading to making of wavefront charts for assumption of linear increase of velocity with vertical time.*

**Clay Deposits of the Denver-Golden Area, Colorado.** KARL M. WAAGÉ. Pp. 373–390; figs. 3. Colorado Sci. Soc. Proc., Vol. 15, No. 9. *Reserves of commercial bodies of refractory clay in Glencairn shale. Member of Purgatoire formation believed low. Brick-clay deposits of Laramie formation believed sufficient for local industry needs.*

**Ohio Geological Survey—Columbus, 1953.**

**Rept. of Inv. No. 15. The Geology of Switzerland Township, Monroe County, Ohio.** THOMAS ARKLE, JR. Pp. 13; figs. 9.

**Rept. of Inv. No. 17. The Meigs Creek No. 9 Coal Bed in Ohio. Part I, Geology and Reserves.** WILLIAM H. SMITH, RUSSELL A. BRANT, AND FRED AMOS. **Part II, Washability Characteristics and Other Properties.** PETER O. KRUMIN. Pp. 163; pls. 7; figs. 97; tbls. 25.

**Aspects of Sedimentation in Lake Waco, Texas.** VICTOR H. JONES AND ROSS E. ROGERS. U. S. Soil Conservation Service, Fort Worth, 1952. Pp. 55; figs. 24; tbls. 13. *Loss of 44 percent of original (1930) reservoirs capacity by 1947 caused by high sediment contribution.*

**Canada Department of Mines—Ottawa, 1952.**

**Mem. 123. Electronic Concentration of Ores with the Lapointe Picker Belt.** C. M. LAPOINTE AND R. D. WILMOT. Pp. 40; figs. 9; tbls. 7. Price, 50 cents.

**Mem. 125. Tin in Canada: Occurrences and Uses.** W. R. MCCLALLAND. Pp. 17; fig. 1; tbls. 3. Price, 25 cents.

**Geology of the Partridge Crop Lake Area, Cross Lake Mining Division, Manitoba.** A. S. DAWSON. Pp. 26. Manitoba Dept. of Mines Pub. 41-1, Winnipeg, 1952.

**61st Annual Rept. of the Ontario Dept. of Mines, Vol. LXI, Pt. 5. Geology of McCool Township.** J. SLATTERLY. Pp. 30; figs. 12. Ontario Dept. of Mines, Toronto, 1953.

**Esquisse Tectonique du Congo Belge et du Ruanda-Urundi.** L. CAHEN. Pp. 4; includes map 1:3,000,000. Ministère des Colonies du Royaume de Belgique, Liège, 1952. *Tectonic outline of Belgian Congo and Ruanda-Urundi.*

**Report on the Geological Survey Department for the Year 1951.** Pp. 135; figs. 9. Geol. Survey of British Guiana, Georgetown, 1952. Price, $1.00. *Annual report including 10 papers on exploration of gold and diamond deposits.*

**Symposium on Diamond Drilling: Trends in Diamond Drilling in the United States.** R. D. LONGYEAR. Pp. 327–343; figs. 10. Chem., Met. Min. Soc. South Africa Jour., April, 1952.

**Venezuelan Petroleum Yearbook—1949.** Pp. 158. Ministerio de Fomento, Caracas, 1951. *Very informative survey of petroleum industry in Venezuela, written both in Spanish and English and well illustrated with many photographs, maps, graphs and tables.*

**Journal of the Royal Society of Western Australia—Perth, 1950.**

**The Geology of the Wattle Flat Area, Chittering Valley.** J. K. GEARY. Pp. 77–107; pls. 2; figs. 4.

**The Geology of the Hamersley Siding Area.** MURRAY H. JOHNSTONE. Pp. 45–75; pls. 3; figs. 10.

**Foraminiferal Investigations in the Perth Basin.** P. J. COLEMAN. Pp. 31–43; figs. 4.

# SOCIETY OF ECONOMIC GEOLOGISTS

## PRELIMINARY ANNOUNCEMENT.

The Fall Meeting of the Society of Economic Geologists will be held in Toronto, Ontario, Canada, in conjunction with the Geological Society of America, Mineralogical Society of America, and others, November 9–10–11, 1953. The Geological Association of Canada will act as hosts.

At these meetings special emphasis will be placed on Precambrian problems, such as correlation, tectonics, alteration, and ore deposits.

Immediately following the technical sessions four field trips of major interest to mining geologists have been arranged:

Field Trip No. 7 will visit the famous Sudbury Nickel Mining District—leaving Toronto 11 P.M., November 11—returning 7 A.M., November 14. Limited to 65 persons—overall cost $46.50.

Field Trip No. 8 will visit the Kirkland Lake and Larder Lake Gold Mining Area—leaving Toronto 6 P.M., November 11—returning 8 A.M., November 14. Limited to 60 persons—overall cost $55.00.

Field Trip No. 9 will visit the Porcupine Gold Area and will leave Toronto 6 P.M., November 11—returning 8 A.M., November 14. Limited to 75 persons—overall cost $53.50.

Field Trip No. 10 will go to Noranda, Quebec, visit that camp and continue eastwards and visit various important mines—leaving Toronto 6 P.M., November 11—returning in the A.M. of November 14 or 15. Limited to 120 persons—overall cost $61.75.

These estimated costs include train fare, berths, hotel, meals and guide books. Both underground and warm outdoor clothing will be required. As the quotas must be adhered to, make your reservations early and avoid disappointment.

All authors who plan to give papers at the 1953 meeting are urged to submit titles and abstracts, as soon as possible, to Olaf N. Rove, Secretary S. E. G., whose address is Mineral Deposits Branch, U. S. Geological Survey, Washington 25, D. C. Closing date for receipt of abstracts in Washington is July 15.

THE PROGRAM COMMITTEE.

ABSTRACTS OF PAPERS PRESENTED AT THE JOINT MEETING OF THE SOCIETY OF ECONOMIC GEOLOGISTS AND THE AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS, LOS ANGELES MEETING, FEBRUARY 16–19, 1953.

## *APPLICATION OF GEOLOGY TO THE DISCOVERY OF ZINC–LEAD ORE IN THE WISCONSIN–ILLINOIS–IOWA DISTRICT.*[1]

ALLEN F. AGNEW.

*U. S. Geological Survey, Denver, Colorado.*

Detailed stratigraphic studies have made it possible to map the minor corrugations that control the zinc-lead ore bodies of the Wisconsin-Illinois-Iowa district.

These zinc-lead deposits occur in the Galena dolomite and the Decorah and Platteville formations of Middle Ordovician age. Detailed lithologic study of the succession of beds permitted subdivision of these three formations into 18 mappable units. Ore is localized as veins along reverse faults and bedding planes; the relation of these ore structures to the limbs of minor corrugations on larger folds was first recognized during extensive detailed mapping of these 18 units in mines.

Mapping based upon outcrop and drill-hole data, and also mapping based only upon grid drillings have been successful in delimiting the ore-localizing structures. More than 15 ore bodies have been discovered from prospecting these structures.

Detailed geologic mapping in the mines as stoping develops has been an aid in following ore shoots that would otherwise have been missed.

Geochemical prospecting has shown that MgO/CaO ratio, heavy metal content, and, locally, percentage of insoluble material increase near ore; these increases may be used as guides to ore.

The U. S. Geological Survey recommended prospecting in the potential ore-bearing zones of the upper part of the Platteville formation. As a result, ore in these zones was found and mined.

## *METHODS USED IN GEOCHEMICAL PROSPECTING ANALYTICAL LABORATORY.*[1]

HAROLD BLOOM.

*U. S. Geological Survey, Denver, Colorado.*

The field tests that have been developed for geochemical prospecting and tried during the past four years, have undergone some changes leading to the improvement of some and the de-emphasis of others.

| Elements | Method | No. determinations per man-day | Sensitivity ppm |
|---|---|---|---|
| Zinc | Dithizone | 100 | 20 |
| Lead | Dithizone | 60 | 10 |
| Copper | Dithizone | 60 | 10 |
| Heavy Metal | Dithizone | 100 | 50 |
| Nickel | Chromograph | 100 | 15 |
| Copper | Chromograph | 100 | 10 |
| Silver | Chromograph | 30 | 0.2 |
| Tungsten | Thiocyanate-stannous chloride | 40 | 10 |
| Molybdenum | Thiocyanate-stannous chloride | 40 | 1 |
| Antimony | Rhodamine B | 40 | 1 |
| Arsenic | Modified Gutzeit | 60 | 10 |
| Manganese | Permanganate | 60 | 50 |

[1] Publication authorized by the Director, U. S. Geological Survey.

The following table shows the elements, methods, productivity and sensitivity in parts per million, of some of the methods in use by the laboratory.

Equipment for running any of these tests costs under $100.00. Over 24,000 determinations have been made for these metals on 11,000 samples during the past year in this laboratory.

## THE DOMESTIC GRAPHITE SUPPLY PROBLEM.[1]

EUGENE N. CAMERON.

*University of Wisconsin, Madison, Wisconsin.*

The United States has depended upon Ceylon and Madagascar for certain grades of graphite for more than forty years. High prices during World War I and subsidies during and since World War II have stimulated production of graphite from domestic sources. Nevertheless, the domestic industry is still not firmly established, and the amounts of usable graphite of various grades available from domestic sources in time of emergency are still uncertain. Because of this situation, domestic graphite resources were reexamined by the Federal Geological Survey during 1949.

At present, Ceylon furnishes "amorphous" lump and chip graphite essential for carbon brushes. Deposits near Dillon, Montana, appear to be the only possible domestic source of this type of graphite. Known reserves in these deposits are small, but additional reserves might be found by exploration.

Flake graphite for use in crucibles and related articles, for packing materials, and for lubricants is obtained chiefly from Madagascar. Deposits in Texas, Alabama, Pennsylvania, and New York contain large tonnages of flake graphite, and certain deposits in these States have been worked at various times since World War I. During this period, however, domestic flake has fared badly in competition with imported flake.

The present paper discusses the problems involved in evaluating domestic graphite resources, the difficulties facing the domestic graphite industry, and the bearing of these matters on the future of the domestic graphite industry and on national policy with respect to strategic graphite.

## GRADING OF NATURAL CORUNDUM ORES.

HOWARD F. CARL, H. W. WHITE, AND ARTHUR HOCKMAN.

*U. S. Bureau of Mines, College Park, Maryland; U. S. Geological Survey, Washington, D. C.; and U. S. Bureau of Standards, Washington, D. C.*

Practical techniques for grading natural crystal corundum have been developed that are based on the abrasive use to which the material is to be put and on the mineralogical composition of the ores.

A grinding value and an index of "toughness," i.e., the rate at which a sample loses its grinding value, are determined by physical methods worked out at the National Bureau of Standards, while the actual corundum content of an ore is assayed by a leach-petrographic technique developed by the Bureau of Mines.

The determination of these three factors have been incorporated into purchase specifications for government stockpiling of natural corundum.

A discussion is presented of the details of the evolution of these techniques and of the manner in which they affect the final grading of ores according to the revised purchase specifications.

## DIMENSION STONE IN THE UNITED STATES IN 1952—A SUMMARY.

CHARLES F. DEISS.

*Indiana University and Indiana Geological Survey, Bloomington, Indiana.*

In 1952, the dimension stone industry exhibited a wide range of alertness and aggressiveness in modernizing its equipment and operating methods. Only a few outstanding producers of granite, marble, limestone, sandstone and slate furnished the leadership for the industry, and even they were not entirely aware of each other's new methods and practices. Many of the stone companies are using inefficient quarry and mill equipment, 25 to 50 years old, and continue to depend on expensive hand labor.

The principal advances in quarrying are 5- to 65-ton mobile cranes, powerlift trucks, tungsten carbide tipped drills, truck haulage instead of rail, quarry-bars and broaching drills instead of chopping type of channellers, and gang-sawing of dimension blocks as first cuts in the quarry. The newer machines and practices in the mills include: fork-lift trucks; floor operated overhead and jib cranes; roller type conveyors; wire saws of single and gang types; newly engineered diamond-saw teeth for single and gang circular saws; hydraulically operated carborundum shaping machines; hydraulic breakers for making split-face ashlar veneer; air-powered carborundum tipped drills, carving tools and hammers; and redesign of plants to eliminate many handling operations.

Building stone manufacturers generally are more aware of competition than the monument producers and are developing more new machines, operations, and by-products. The more successful by-products are chicken grit, concrete aggregate, and mineral fertilizer from granite waste, and whiting, chemical calcite, agricultural limestone, and other uses of pulverized marble and limestone. Split-face ashlar veneer for domestic housing is the outstanding development of the Indiana limestone industry.

## GEOCHEMICAL ASSOCIATION OF NIOBIUM (COLUMBIUM) WITH TITANIUM AND ITS ECONOMIC SIGNIFICANCE.[1]

MICHAEL FLEISCHER.

*U. S. Geological Survey, Washington, D. C.*

Niobium occurs in highest concentrations in granitic pegmatites and in alkalic rocks such as the nepheline syenites. It occurs commonly as a substitute in titanium minerals. The weathering of alkalic rocks produces bauxite enriched in niobium. Analyses show Arkansas bauxite to contain an average of 0.05% Nb; the niobium present in the Arkansas bauxite processed annually is about 80% of the amount imported annually by the United States. Fractionation of black sand from Arkansas bauxite showed the niobium to be concentrated chiefly in the ilmenite fraction containing over 40% $TiO_2$ and up to 0.86% Nb.

Analyses of titanium minerals show the presence of nicobium, the amount present depending largely on the type of host rock. Material from alkalic rocks and from granitic pegmatites is highest in niobium contents.

The need for metallurgical research, especially on the possibility of recovering niobium and titanium from chlorination processes, is pointed out.

## A HALF CENTURY OF DIMENSION GRANITE QUARRYING IN MASSACHUSETTS.

RALPH A. FLETCHER AND WILLIS P. MOULD

*H. E. Fletcher Company, West Chelmsford, Massachusetts; and Mining and Quarrying Associates, Keeseville, New York.*

Quarrying is a phase of mining given scant attention by mining engineers. The more important quarrying areas of Massachusetts are West Chelmsford, Quincy and Milford.

Developments in transportation have been of vital importance in the cycle of opening, growth, extinction and rebirth of quarrying districts.

The basic problems of quarrying whole stone from the solid ledge is unchanged over the ages. The most baffling and costly single problem is still the release of internal stresses inherent in solid formations of ledge material.

New techniques, new machinery and new tools and materials have eased the demands on human effort, increased production, and decreased waste. Developments in artificial abrasives, the wire saw, and jet-piercing are producing a revolution in quarrying dimension stone.

## COMMERCIAL SYNTHESIS OF STAR SAPPHIRES AND STAR RUBIES.

CLIFFORD FRONDEL.

*Harvard University, Cambridge, Massachusetts.*

The varieties of natural corundum called ruby, sapphire, star ruby and star sapphire have been prized as gemstones since ancient times. Most of the natural material is obtained from Ceylon, Burma, Siam and India. Corundum can be synthesized by crystallization from highly aluminous silicate melts, by the reaction of halogen compounds of aluminum with water or boric oxide in the vapor phase at high temperatures, and in other ways. Large single-crystals of corundum of high quality, suitable for both gem and technical applications, were first synthesized on a commercial basis in 1908 by the Verneuil process. Basically, this method involves direct crystallization from a melt prepared by dropping particles of pure aluminum oxide through an oxyhydrogen flume held at about 2000° C. The molten droplets fall upon a relatively cool support of fire clay or corundum where they crystallize and slowly build up a rounded single-crystal of corundum called a boule.

The asteriated varieties of ruby and sapphire were first synthesized in 1947 by the Linde Air Products Company and are now produced commercially on a large scale. The asterism is produced by the exsolution in oriented position of rutile needles from an initially homogeneous solid solution of titanium in corundum single-crystals grown by the Verneuil process. The rutile inclusions are oriented at right angles to the c-axis of the corundum in three equivalent positions intersecting at 120°. Incident light is reflected and scattered selectively in directions perpendicular to the elongation of the inclusions, and gives rise to the visible star seen in properly oriented cabochon stones out from the boules.

The initial solid solution contains about 0.06 to 0.2 atomic percent of trivalent titanium in substitution for aluminum, together with about 1.4 percent chromium and about 0.3 percent ferric iron as pigmenting material in ruby and sapphire, respectively. The clear, homogeneous boules are annealed at about 1900° to remove strain, and are then heated for 2 to 72 hours in an oxidizing atmosphere between 1500° and 1100° to induce precipitation of rutile, $TiO_2$. Precipitation does not occur over about 1500°, and exsolved rutile can be dissolved by heating to somewhat over 1500°.

The history of the synthetic corundum industry is reviewed, and production statistics are cited.

## *MINING AND MILLING OF LITHIUM PEGMATITES AT KINGS MOUNTAIN, NORTH CAROLINA.*

E. R. GOTER, W. R. HUDSPETH, AND D. L. RAINEY.

*Foote Mineral Company, Kings Mountain, North Carolina.*

The first reported mining interest in the Kings Mountain, N. C., area was during the period from 1880 into 1920 when several unsuccessful attempts were made to mine cassiterite. Although known to exist, the spodumene deposits attracted little attention until early in World War II, when demand for lithium highlighted the need for domestic ore reserves.

Encouraged by Federal agencies, the Solvay Process Company operated a concentrating plant at Kings Mountain from 1942 until 1946. During this time, extensive prospecting by Solvay indicated substantial spodumene deposits, but the drop in demand for lithium chemicals closed the plant for several years.

To assure a domestic source of lithium ore, Foote Mineral Company acquired the Solvay interests in 1950, and after extensive renovation and with a new process started production in July 1951.

Present quarrying operations are in an area north of the Solvay diggings on a dike about 300 feet wide and over 1000 feet long. Stripping and mining operations are carried on simultaneously, with the shovel operator sorting the ore before loading. Dumping over a scalping grizzly removes most of the remaining dirt. Wagon drills and jack hammers are used for bench drilling and stripping. Two 1½ cubic yard shovels are used to load the 10-ton GMC's for the haul to the jaw crusher.

The minus 3-inch crusher product is conveyed to a ¾-inch screen which delivers undersize to a storage bin. Oversize is reground in a hydrocone crusher. This crushed ore is belt fed into two 6 by 8 feet pebble mills equipped with trommels clothed with 40-mesh screen. Oversize in the mill discharge is returned by an Esperanza drag.

Screen undersize from the mill, about 15 percent solids, is deslimed in a hydrocyclone and fed into 5-turn spirals where 5 percent heavy mineral concentrate is removed. This by-product is further concentrated into a mixture of cassiterite, columbite and tantalite on a Deister table. In addition to these by-products, there are fairly sizeable percentages of feldspar, mica, and beryl in the pegmatites, but to date it has not proved commercially economical to separate them.

The rejects from the 5-turn spirals are laundered to a classifier, thence to two conditioners which operate in series at about 55 per cent solids. Amine, caustic, dextrine, and pine oil are added as reagents and the discharge is diluted to 25 percent solids before delivery to a bank of flotation cells. In this separation, the underflow is the spodumene concentrate which is pumped to Allen cones, dewatered and delivered to storage. The rougher gangue froth containing 7 percent spodumene is scavengered in a bank of Morse-Weining cells and further concentrated on a Deister table before going to storage.

Concentrates drain to about 95 percent solids on the storage pads and then are dried in a rotary kiln. Ceramic-grade spodumene is passed over an induced-roll type magnetic separator, where iron and iron bearing minerals are removed. The dried product is trucked to a nearby railhead where a conveyor belt bucket system is used to bulk load both hopper and box cars.

Trailing disposal is conventional, with an earthen dam and Weir type overflow which is raised by by adding sections of concrete pipe as necessary.

Repair, maintenance and construction work is organized as a separate department under the Plant Engineer. Safety is handled by an Employee Welfare Supervisor with regular monthly meetings and regular inspection by a Safety committee.

Construction has begun on facilities which will raise capacity from 360 tons to 1,000–1,200 tons per day. These changes include a larger primary crusher, new rod mills, larger classifiers and spirals, together with two new banks of flotation cells. The new mill equipment will be set up in two parallel circuits, each capable of handling 500–600 tons per day, thus assuring partial production in the event of equipment failure.

## *SOME RECENT AMERICAN DEVELOPMENTS IN GEOCHEMICAL PROSPECTING FOR MINERALS.*[1]

H. E. HAWKES.

*U. S. Geological Survey, Denver, Colorado.*

Developmental research and practical application of geochemical methods of prospecting for minerals have been progressing rapidly since the last general progress report at the San Francisco A. I. M. E. meetings four years ago. New or improved chemical procedures developed by the Geological Survey will be discussed in the paper by Harold Bloom. Experimental field projects have been conducted by the Survey in ten major mining districts in the United States; six other Survey field projects are in progress. At least 25 privately sponsored geochemical prospecting crews are active in the United States at the present time. Geochemical soil surveying has been most generally effective, and has assisted materially in several major discoveries. Botanical methods have been successfully applied in one major district. Studies of traces of epigenetic metals in rocks adjoining or overlying ore deposits show promise in a wide variety of geological environments. The distribution of traces of metals resulting from upward migration of metal from bedrock sulfides also shows promise where the bedrock is buried beneath a blanket of glacial or alluvial material.

## *A "FOSSIL" GEOCHEMICAL ANOMALY NEAR JEROME, ARIZONA.*[1]

L. C. HUFF.

*U. S. Geological Survey, Denver, Colorado.*

The Precambrian copper deposits at Jerome, Arizona, and their enclosing metamorphic rocks are overlain unconformably by the Tapeats sandstone of Cambrian age. Samples of the Tapeats sandstone were analyzed to determine if copper eroded from these ore deposits was incorporated in the Tapeats sandstone as it was deposited. Trace analyses of these samples reveal anomalous copper concentrations of more than 100 parts per million in the basal Tapeats sandstone throughout an area extending at least two miles from Jerome in contrast to a background elsewhere of about 20 parts per million. Anomalous zinc concentrations of more than 100 parts per million are distributed in roughly the same area as the copper, but abnormal lead concentrations are limited to the immediate vicinity of the mines.

The geochemical anomaly in the Tapeats sandstone is interpreted as a feature formed as the sandstone was deposited. By comparison with geochemical anomalies exhibited in residual soil, in alluvium, or in other sediment of Recent geologic age, the preserved anomaly in the Tapeats might be considered a "fossil" anomaly. The search for such geochemical anomalies may offer a new approach to prospecting areas in which the ore-bearing formation is covered unconformably by younger sediments.

## ROCK BURSTING AND OTHER GEOLOGIC PROBLEMS IN THE GRANITE QUARRIES AT BARRE, VERMONT.[1]

RICHARD H. JAHNS.

*California Institute of Technology, Pasadena, California.*

The large granite quarries of the Barre district, in central Vermont, have been developed in a highly irregular, cross-cutting intrusive mass that is enclosed mainly by noncalcareous metasedimentary rocks. This mass comprises numerous elongate, subparallel lobes that are separated by relatively thin screens of country rock. The three largest lobes are 600 to 1,500 feet in breadth and 1½ miles or more in exposed length.

Outcrops and quarry exposures reveal widespread sheet structure and several well defined types of primary joints. The thickness and attitude of the granite sheets appear to be related to glacial erosion, whereas the distribution and attitude of the joints are related to contacts between granite and country rocks. In general, those masses of granite with the fewest natural fractures have been most susceptible to rock bursting, which has been most common in the interior parts of the largest intrusive lobes, and at localities where glacial erosion was relatively severe.

Granite that is marred by "sap," a faint discoloration or darkening that "deadens" the appearance of the stone, is especially abundant in areas where many sheet fractures are present. Development of this and other types of discoloration can be related to glacial erosion and to groundwater circulation during the Quaternary period.

Higher yields of usable granite might be obtained from new quarries at points where geologic conditions are relatively favorable, and the spoilage of stone in existing quarries by rock bursting and other uncontrollable breaks probably could be reduced through minor modifications in quarrying practice.

## BERYL DEPOSITS IN THE HARDING PEGMATITES, TAOS COUNTY, NEW MEXICO.[1]

RICHARD H. JAHNS AND JOHN W. ADAMS.

*California Institute of Technology, Pasadena, California; and U. S. Geological Survey, Denver, Colorado.*

Several remarkable deposits of coarse-grained beryl have been discovered since 1943 at the Harding lithium-tantalum mine, in northern New Mexico. Small-scale operations, based on recovery by hand sorting, have yielded 350 tons of high-grade concentrates and an additional 150 tons of lower-grade material during the period 1950–1952. The gross value of this output is approximately $125,000.00.

The principal occurrences are in the largest pegmatite dike, which at the mine is 45 to 80 feet thick and dips southwest at an average angle of about 10 degrees. It is strikingly layered, or zoned, and three general types of beryl deposits can be distinguished in terms of the zonal structure.

Large anhedral crystals of white and very pale greenish-to-pinkish beryl occur with quartz, albite, perthite, muscovite, and apatite in a 6-inch to 8-foot layer immediately beneath the hanging wall of the dike, and in a similar layer above the footwall. Many of these crystals have dimensions measurable in feet. The richest concentrations are in the upper layer, and are defined by hanging-wall rolls that plunge very gently west-southwest. Beryl forms about 5 to 12 percent of the major shoots.

Smaller anhedral-to-subhedral crystals of white-to-pinkish beryl occur farther from the walls of the dike, generally with quartz, spodumene, perthite, and albite. Though locally abundant, they form no very large concentrations.

Euhedral crystals of very pale pinkish to yellowish beryl, generally an inch or two in maximum dimension, form small but rich concentrations in the central part

of the dike. Many of them are associated with albite and smoky quartz, and appear to have developed along fractures in massive quartz.

All varieties of the beryl contain moderate amounts of cesium and other alkalis, and their BeO content ranges from 11.0 percent to about 12.5 percent.

## *SOME GEOLOGIC FEATURES OF A POTASH DEPOSIT.*[1]

C. L. JONES.

*U. S. Geological Survey, Carlsbad, New Mexico.*

Geologic investigations in the Carlsbad district of New Mexico have yielded information on distinctive features of potash deposits and distribution of potassium minerals in the saline sedimentary rocks of the Salado formation of late Permian age.

The Salado formation is divisible into three distinct lithologic groups: chloride, sulfate, and clastic. Two lithologic subtypes are recognized in the chloride group: (a) halite beds containing various amounts of quartz and silicate minerals of clastic origin and (b) halite beds containing no minerals of clastic origin. In the sulfate group the materials forming clearly defined stratigraphic units are anhydrite, glauberite, polyhalite, and kisserite. Each stratigraphic unit or bed in this group commonly shows systematic changes in mineral composition, which ranges from an anhydrite facies through polyhalite to a kieserite facies. The clastic group is represented by thin, persistent beds of clay, silt, and sand, which are traceable throughout the district.

The potassium minerals are found as: (1) accessory minerals in the chloride, sulfate, and clastic groups of sediments; (2) secondary masses either replacing or displacing a rock that may belong to any one of the three lithologic groups; and (3) bedded deposits in either the chloride or the sulfate group. All potassium minerals common in saline sedimentary rocks have been recognized in bedded deposits in the chloride group. The deposits are generally restricted to the halite beds containing silicate minerals of clastic origin. Polyhalite is the only potassium mineral that occurs as a bedded deposit in the sulfate group.

The bedded deposits in the chloride group are of present economic importance. The deposits, confined to definite stratigraphic units, consist of an admixture of halite, a small amount of clastic material, and potassium and associated magnesium minerals. The potash deposits are shown on maps by means of isopleth contours representing the variations in potassium content in a single stratigraphic unit. The regional distribution of this potassium content has not been correlated with any recognizable stratigraphic or structural feature of the unit or its geologic environment. Abrupt lateral variations in mineralogy are characteristic of the deposits. The variations may be shown quantitatively by means of mineral-facies maps.

## *QUARRY PRACTICES IN THE INDIANA BUILDING STONE INDUSTRY.*

RICHARD P. LETSINGER.

*Victor Oolitic Stone Company, Bloomington, Indiana.*

Indiana Limestone is quarried by the open pit method. The first operation is to determine the commercial value of a deposit at a designated place. This is done by core drilling, which means taking samples of stone at varying depths over a specified area. The machine used is a core drill, which extricates a cylindrical length of stone about four inches in diameter and eight inches long.

Removal of overburden is the next operation. If the overburden is heavy, powder blasting is used to loosen it. This waste is removed to expose the solid stone deposit. Blasting must be carefully supervised in order to not fracture the limestone beneath. Fractured stone is rejected for commercial dimension stock.

After the overburden is removed, channeling machines are moved onto the solid ledge of stone. Derricks are erected to handle the quarried blocks.

A channeling machine operates steel bits which drive continuously into the stone while the machine moves forward and backward on a track. The depth of the cut may be as much as fourteen feet. Bits are mounted on both sides of the machine for running a double cut which is customary.

## *MONAZITE DEPOSITS OF THE SOUTHEASTERN ATLANTIC STATES.*[1]

JOHN B. MERTIE, JR.

*U. S. Geological Survey, Washington, D. C.*

Monazite is the principal mineral from which the cerium earths and thorium are obtained. Fluviatile monazite placers were mined in the piedmont of North and South Carolina from 1887 to 1911, but competition with the deposits of Brazil and India finally terminated domestic mining. Recent restrictions on the exportation of monazite from foreign countries have made this mineral a scarce commodity. Large reserves are present in Idaho and in the Southeastern States. The monazite of the Southeastern States has average tenors of 63.20 percent in the rare earths, 5.67 percent in $ThO_2$, and 0.38 percent in $U_3O_8$.

Monazite placers were known, during the era of mining, to extend for about 100 miles along the regional strike of the crystalline rocks. A preliminary sampling of these deposits was done in 1945. Monazite in bedrock has now been traced northeastward and southwestward from the sites of placer mining in a so-called western belt that extends 600 miles from east-central Virginia to east-central Alabama. An eastern monazite belt has also been discovered and traced for 200 miles from the vicinity of Fredericksburg, Va., to a site southeast of Raleigh, N. C., with a possible continuation in South Carolina.

Precambrian granitic rocks are believed to have been the original sources of this monazite, which now occurs in rocks of several kinds and ages, including orthogneiss, paragneiss, granitic intrusives, pegmatites, and granitized and pegmatized country rocks. Evidence accrues that the gneisses are the principal host rocks. The monazite belts do not everywhere follow the regional strike of the crystalline rocks, and granitic rocks that are monazite-bearing within the belts are barren outside the belts. The linear collocation of the belts is explained by a postulate that Precambrian monazite-bearing fluviatile deposits were formed in two major valleys, that these deposits were preserved in one or more geosynclines, and that the present monazite-bearing rocks have been derived from the Precambrian intrusives and fluviatile deposits by regional metamorphism, differential remelting and granitization.

## *DIMENSION STONE INDUSTRY OF CALIFORNIA.*

L. A. NORMAN, JR.

*California Division of Mines, San Francisco, California.*

The relatively small annual production of dimension stone in California belies the important contribution of this industry to urban and metropolitan development in the state from earliest times. Value of the total recorded output from 1887 to 1950 approximates 40 million dollars, of which 77 percent represents granitic rocks. Sandstone, marble, limestone, slate, volcanic rocks, and some serpentine, travertine, and onyx marble account for the remainder.

Wide fluctuations in annual production are characteristic. During recent years the average value of the annual output, about one-third million dollars, reflects a

sharp decline from the 1925 high of two million dollars. In 1950, California ranked 14th among the states in value of dimension granite produced.

Present activity is greatest in operations for granite, most of which is used for monuments, building veneer, and surface plates. "Black granites" (dioritic and gabbroic rocks) represent one-third of the annual production; they constitute the most important monumental stone, and are finding an expanding market as surface plates. Also significant are the search for, and marketing of, an increasingly wide variety of stone for contemporary western buildings and landscaping.

Satisfactory sources of quality stone are available, and the major problem of the industry is to establish wider acceptance of its products in the face of keen competition from imported stone and artificial materials. Continued attacks on this problem should include increased diversification and standardization of products, search for equipment and methods to reduce quarry, shop, and distribution costs, and improved quality control through field and laboratory studies. Also desirable is a more organized effort to publicize the inherent qualities of natural stone and to place essential illustrated data before present and potential consumers and designers. California's swelling population, attendant industrial growth, and unprecedented building activities offer a challenge and a promise to the dimension-stone industry of the state.

## *PETROLOGY OF THE SALEM LIMESTONE (INDIANA BUILDING STONE).*

JOHN B. PATTON.

*Indiana Geological Survey, Bloomington, Indiana.*

South-central Indiana produced 60 percent of the dimension limestone quarried annually in the United States. The quarried beds, part of the Salem limestone (Mississippian), are buff and gray, massive, granular, cross-laminated, high-calcium limestone, and are composed largely of small fossils and fossil fragments.

In order of their abundance, the mineral contituents are calcite, dolomite, quartz, chert, clay minerals, limonite, hematite, pyrite and leucoxene. Calcite is the principal constituent but locally dolomite and chert are common to abundant. Most of the calcite and some of the quartz was primary. The remaining mineral content is secondary and was deposited by ground water or altered from primary grains of magnetite and ilmenite, which generally are no longer identifiable.

The most abundant fossils are *Endothyra baileyi*, sections of small crinoid stems, and bryozoan fragments. In some zones the particles are coated with calcite, but true oolites are rarely found. Most of the fossil particles are microcrystalline calcite (less than .01 mm), but some have recrystallized so that each fragment consists of a single crystal. Grain size ranges from 0.1 mm to 1.5 mm, and averages about 0.7 mm.

Calcite, and in places dolomite, is the cementing material. Calcite crystals in the cement commonly are as broad as the pore space, but dolomite in the cement is microcrystalline.

In addition to the facies used for building stone, the Salem contains beds of drab-brown, fragmental, impure limestone that contain larger percentages of dolomite, quartz, pyrite, and limonite. This impure facies occurs most commonly at the top of the formation but may occur beneath or interbedded with the building stone.

The Salem is bioclastic in origin and shows a high degree of size-sorting. Deposition was controlled by marine currents and wave action, and fossil content was thus determined largely by particle size rather than by the character of the local organic life.

## ACCUMULATION OF MINOR-ELEMENTS IN COAL ASH AND ITS ECONOMIC IMPLICATIONS.[1]

TAISIA STADNICHENKO.

*U. S. Geological Survey, Washington, D. C.*

This is a progress report of a study begun four years ago with the collection of columnar coal samples and the determination of minor and dispersed elements in the ash. The work was extended from the central part of the Appalachian region (Pennsylvania, Ohio, West Virginia, and Virginia) to the Great Northern Plains (Wyoming, Montana, and North Dakota), Rocky Mountains (Colorado, Utah, and New Mexico) and the eastern part of the Interior Province (Indiana, Western Kentucky). Eventually, the Geological Survey plans to examine all outstanding producing coal beds of the United States. Quantitative spectrographic analysis of coal ash samples was expanded from five elements originally studied (Be, V, Ga, Ge, and Sn) to fifteen elements (Be, B, Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Y, Mo, Sn, La).

The largest accumulations of V, Cr, Co, Ni, Cu, Zn, Ga, and Ge have been found in the ash of lignites (Early and Late Cretaceous age) of the Atlantic Coastal Plain. Some of the kettle bottoms and coalified trunks preserved in clay, sandstone, and shaly roofs of coal beds also showed large concentrations of germanium and other minor elements.

Although the character and manner of accumulation of the minor elements have not been sufficiently studied to give a clear picture of the process, the available data indicate that the largest accumulations are found in woody coals. Fusain, or mineral charcoal, much of which has been derived from the woody plants, is, on the contrary, poor in minor elements. Apparently the secondary mineralization of these remains by carbonate, silica, and iron-rich waters and solutions carrying suspended paticles of clayey material, led to a loss of minor elements, partly by dilution and partly by replacement.

The development of a spectrophotometric method using phenyl fluorone permits the rapid determination of germanium present in amounts below the limits of our quantitative spectrographic method. Since all analyses of ash invariably show larger concentrations of other elements in germanium-rich samples, we intend to use the phenyl fluorone method for preliminary examination in selecting samples for the quantitative spectrographic determinations.

Flotation tests with coals showed that most of the minor elements can be concentrated in the ash of the lighter fractions (float 1.32 sp. gr.), and zinc largely concentrates in the heavier fractions (sink 1.32 sp. gr.).

The largest concentrations of germanium, an element much needed in the development and production of crystal diodes, transistors, rectifiers, and other electronic devices, have been found in coals of Allegheny formation (Lower and Middle Kittanning beds) of northeastern Ohio.

## USE OF GEOLOGY IN DEVELOPING THE BLACKBIRD COBALT-COPPER DEPOSITS, IDAHO.[1]

J. S. VHAY.

*U. S. Geological Survey, Spokane, Washington.*

A brief discussion of the geology of the Blackbird district, Idaho, emphasizes the importance of plunge in the shapes of the cobalt-copper deposits formed by replacement along shears in strongly metamorphosed rocks of the Belt series.

The use of geology in developing these deposits is considered under two headings: (1) what might have been used but was not, for several reasons; and (2) where geology was used to advantage.

Geochemistry was not used during early development because no information was available. Recently geochemistry has shown an area of background higher in cobalt to which future prospecting can be limited. If the plunge of ore had been appreciated, the sites for drilling could have been better selected and some dry holes could have been avoided.

During 3 years of underground development with little geologic direction, some of the work was not to best advantage because the importance of the faulting was not realized, the plunge and echelon arrangement of the ore bodies were not appreciated, and at times the ore was not recognized.

Geology and geochemistry have been extensively used more recently in the district. Hot spots found by geochemical testing have guided some current development, and probably will guide future work. Geology is much used now in planning development as well as mining. Stopes and other workings are carefully mapped, a model of the complicated Brown Bear area is kept up to date, and the deposits are stoped up the plunge.

## *SKETCH OF THE GEOLOGY AND ORE DEPOSITS OF BAJA CALIFORNIA, MEXICO.*

EDWARD WISSER.

*University of California, Berkeley, California.*

Probably in late Lower Cretaceous time, a great composite batholith invaded Baja California and southernmost California. Intrusion was preceded or accompanied by strong folding and metamorphism of late Paleozoic, Triassic, Jurassic and Lower Cretaceous sediments and volcanics, and was followed by formation of scheelite, iron, copper, precious-metal, sparse lead-zinc and a few manganese deposits.

During Upper Cretaceous, Paleocene and Eocene time the western flanks of the Peninsula were mainly submerged and covered with sandstone and shale, but at the close of the Eocene vigorous uplift on the east dragged the western part up with it above sea level, only to subside again in Miocene time.

In the late Miocene an elongated uplift occupied the site of the present Gulf of California, with the present Peninsula forming the western slope. A thick series of flows and pyroclastics, the Comondú volcanics, poured out from the crest of the uplift, their vents probably lying along fissures paralleling the crest.

The uplift continued after Comondú time, and the great graben which is now the Gulf of California probably started to drop between two systems of graben faults on either side of the Gulf. Slivers along the east coast of the present Peninsula were depressed to receive Pliocene sediments and tuffs, within which were deposited manganese oxide as veinlets and replacements, as well as the Boleo disseminated copper. The alignment of these presumably hypogene deposits, just west of the western zone of graben faults, suggests that the ore-bearing solutions rose along fissures connected with the fault zone, although the main dropping of the graben occurred in Pleistocene time.

## *GENESIS OF CALIFORNIA TALC.*

LAUREN A. WRIGHT.

*California Division of Mines, Los Angeles, California.*

The three talc districts of eastern California contrast with one another in geological setting, and in the nature and origin of their respective deposits. Talc-tremolite bodies near Silver Lake are part of an Archean (?) meta-sedimentary sequence extensively invaded by basic to acidic bodies. A 4-stage metamorphic history is indicated: 1) a temperature increase, to perhaps 600° C to 700° C, producing

diopside-calcite-quartz-feldspar-garnet hornfelses and forsterite marbles from silica-rich and silica-poor carbonate strata, respectively; 2) a temperature decrease to well below 500° C, hydration and magnesia metasomatism to cause tremolitization of certain marble layers and later development of serpentine in magnesian units; 3) a probable temperature increase to plus 500° C, renewed tremolitization concurrent with the emplacement of pegmatite; 4) a temperature decrease and formation of talc, mainly as a stress mineral in tremolite rock. The additive MgO, $SiO_2$, and $H_2O$, introduced mainly during the first period of tremolitization and probably during the emplacement of the largest granitic bodies, may all be of magmatic origin. MgO may have been derived in the granitization of magnesian strata.

Talc deposits of the southern Death Valley-Kingston Range region are silicated carbonate strata of the Algonkian Crystal Spring formation, and exist at or near the margins of diabase sills. The deposits contain carbonate minerals, tremolite, serpentine, and talc, each formed partly at the expense of each listed before it, and probably under successively lower temperatures. The persistence of a calcite-tremolite association under the highest temperatures, together with evidence that intrusions were shallow, indicates temperatures and pressures distinctly lower than the maximum for the Silver Lake deposits. MgO and $SiO_2$ appear to have been derived from the diabase magma, but ground water in the original sediments may have facilitated the alteration and supplied MgO.

Talc deposits of the Inyo Range are alterations mainly of Ordovician and Silurian dolomites and quartzites. That even tremolite is a rare associated mineral suggests still lower maximum temperatures. Much or all of the additive MgO and $SiO_2$ was apparently derived from the enclosing sediments.

# SCIENTIFIC NOTES AND NEWS

THE BILLINGS GEOLOGICAL SOCIETY of Billings, Montana, will hold its fourth annual conference during the first portion of September 1953, in the Little Rocky Mountain Area of northcentral Montana. Headquarters and registration will be at Zortman, Montana. Two days will be spent on Little Rocky Mountain sections extending from the Precambrian to the Upper Cretaceous, including the type locality for the Lower Mississippian. Participation will be limited to 200. Paul McGovney, Geologist for Honolulu Oil Corporation at Billings, is General Chairman for the field conference. John M. Parker, Geologist for George Greer, Trustee, at Billings, is editor. All persons interested should write immediately to J. L. Cramer, Stanolind Oil and Gas Company, 526 Securities Building, Billings, Montana.

M. S. SMERCHANSKI, Consulting Geologist for the Lake Lingman Mining Company, has been elected a member of the Board of Governors of the University of Manitoba.

STANLEY H. CATHCART died on March 19th at his home in Harrisburg, Pa.

Research workers in the fields of mineralogy, petrology, paleontology, and geology are invited to apply for admittance to a course in autoradiography to be given by the OAK RIDGE INSTITUTE OF NUCLEAR STUDIES from June 15 to 25. The microscopic analysis of alpha tracks in a photographic emulsion enables one to locate and measure the amount of uranium, thorium and other alpha-emitting elements in minerals and paleontological specimens. Although rather widely employed in Europe, mineral autoradiography is relatively new in this country. Frank Hoecker, Professor of Physics, University of Kansas, and R. H. Herz, of Eastman Kodak, Ltd., London, will discuss and demonstrate several aspects of alpha track autoradiography during the course. Eight other specialists will lecture on and demonstrate other phases of autoradiography. Additional information on the course may be obtained from the Special Training Division, Oak Ridge Institute of Nuclear Studies, P. O. Box 117, Oak Ridge, Tennessee.

Geologists, representing 13 midwestern universities, met on February 28 at the MIDWEST INTER-LIBRARY CENTER in Chicago to explore possibilities for the cooperative acquisition of foreign geologic maps and files of minor and less-used journals, particularly those of foreign academies, such materials to be acquired by and housed at the Center for the joint use of the several institutions.

WALLACE G. FETZER, Geologist with Vanadium Corp. of America at Durango, Colorado, is now with Oglebay, Norton & Company, in Duluth.

EDMUND C. HARDER, Montreal, senior Geologist for Aluminum, Ltd., and subsidiaries since 1928, has been appointed a member of the board, succeeding the late Hon. Leighton McCarthy.

FRANCIS CAMERON, vice-president, was elected to the board of St. Joseph Lead Company, New York, succeeding George H. Love who resigned.

JOHN A. HIPPLE, chief of the atomic section, National Bureau of Standards, Washington, D. C., has been named director of the Mineral Industries Experiment Station at the Pennsylvania State College. The appointment, which became effective March 1, fills the vacancy created by the retirement on December 15 of DR. ALFRED W. GAUGER. He had served for 21 years on the faculty. A native of Lancaster, Dr. Hipple attended Franklin and Marshall College and Penn State and then went to Princeton University for graduate training in physics. He received his doctor of philosophy degree there in 1937.

ROY L. RAY, of Houston, and KARL DYK, of Tulsa, have been named president and vice-president, respectively. BART W. SORGE, of San Gabriel, California, secretary-treasurer, and MILTON B. DOBRIN, of Dallas, the new editor of the Society of Exploration Geophysicists. Their election was announced by CURTIS H. JOHNSON of Los Angeles, retiring president.

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ERRATA, Number 3—Page 166, "Figure" should read Table 1

Page 168, "Sederhom" should read Sederholm

Page 171, "$CO_3^{18}$" should read $CO_3^{18=}$